

D.N. TRIFONOV

THE PRICE OF TRUTH

The Story of Rare-Earth Elements

Short Introduction

This book is about a fascinating family of chemical elements.

Popular science writers generally tend to overuse the word “fascinating” but in this case it gives a very apt description. Indeed, everything about these dozen and a half elements is fascinating—the histories of their discoveries, their properties and their applications.

Take Mendeleev’s periodic table of elements. The row under the table describes 14 elements from cerium to lutetium. When we add to them lanthanum, yttrium and scandium which are found in the third group of the table we have 17 elements comprising this fascinating family.

Seventeen? Was not it a dozen and a half just a few lines above? What is it—a slip or carelessness?

Not at all. There is yet no complete agreement on which elements can be called the rare-earth elements. We shall discuss this problem below.

At last we gave the name to this family—the rare-earth elements belong to it. This rather interestingly sounding name contains two substantial errors.

First, let us find out the origin of this name.

In those remote times when chemistry was just emerging as a science among those few concepts it started with was the concept of “earth”. Chemists gave this name to the compounds which revealed

alkaline properties—did not melt or change the appearance upon moderate heating, were hardly soluble in water and did not evolve gas bubbles upon interaction with acids. All “earths” were assumed to be individual chemical elements.

Now it is clear that in fact the “earths” were oxides of some, now well-known, metals, namely magnesium, calcium and barium.

All the so-called rare-earth elements were first discovered and isolated in the form of oxides. Early studies demonstrated that these oxides exhibited characteristic features of the “earths”, that is, that they were the “earth” elements. In addition, the minerals that contained them were rather rare so that it is not surprising that the elements were called “rare”.

Thus, the name “rare earths” has survived until our days as one of anachronisms of chemistry.

Modern geological and geochemical data show that these 17 elements are not really rare. On the whole, their share is greater than that of those apparently common metals as lead, silver or mercury. More than 250 rare-earth minerals are known at present.

Indeed, these elements are not all that rare.

Further studies demonstrated that the properties of these elements differed from those of the classic “earth” elements. Then their oxides should not be called earths.

We see that the name “rare earths” is just a relic of the past still used owing to a tradition. Sometimes it is better to keep an old familiar name, even if it has lost its former meaning, than invent a new one. Though this family of elements never lacked for names as we shall see in this story.

Now let us clearly specify the names to be used in the book.

The rare earths are the oxides of yttrium, scandium, lanthanum and 14 next elements.

The metals forming these oxides are the rare-earth elements. We shall use the old-fashioned term "rare earths" in our history of the discovery of these fascinating elements.

Their history cannot be compared to the history of any other chemical elements—it is so confusing, enthralling and full of unexpected twists.

Even the seemingly obvious concept "the discovery of a chemical element" becomes rather less than obvious in the case of the rare-earth elements. The dates of discoveries of some rare-earth elements given in the best encyclopedias and handbooks can be wrong.

The fate of one of the rare-earth elements is so unusual that we devoted a special chapter to it in this book. Now it is known as promethium.

The rare-earth elements make up about $1/6$ of all the elements on the Earth. But it is not a wild exaggeration to say that it gave to chemists no less trouble than the other $5/6$. Tens and hundreds of scientists took on themselves the hard and thankless task of studying the rare-earth elements, their work required unlimited patience and did not promise spectacular results. The basic difficulty was that the rare-earth elements were extremely similar in their chemical properties. Even now in the age of highly sophisticated experimental techniques it is not easy to isolate individual rare-earth elements from a mixture of them (they are found all together in nature). How much more difficult it was for chemists of past generations in their home laboratories equipped with primitive apparatus.

A prominent French chemist Georges Urbain once gave a very imaginative description of the history of rare-earth elements saying: "It was a sea of errors and the truth sank in it."

But when the truth had been finally uncovered, when all intricacies of rare-earth elements had been studied it became clear that they were priceless, indeed. Rare earths make their contribution to the progress in practically all branches of modern technology.

Here we end this short but necessary introduction and begin our story.

The Thorny Path of Discoveries

Each problem in science has its origin. Sometimes it is quite obvious and presents no difficulties in affixing the exact date to it. For instance, we know that the periodic law was discovered by Dmitri Mendeleev on March 1, 1869 and that radioactivity was discovered by the French physicist Henri Becquerel on March 1, 1896.

But what was the origin of the story of rare earths? The historians of chemistry have different views on that. We shall not analyze them but just present the most widely accepted one.

A mineral from an abandoned quarry. On the two-hundred-year-old maps of Sweden one could see the name Ytterby—apparently, it was a small village which had left no significant trace in the history of Sweden.

But it is in the history of rare-earth elements that Ytterby holds a distinguished place. Suffice it to say that four rare-earth elements—yttrium, terbium, erbium and ytterbium—were called in its honour.

...The Swedish army lieutenant Carl Arrhenius was an amateur mineralogist. In the summer of 1787 he hunted for new minerals for his collection in an abandoned quarry near Ytterby and he was lucky, indeed. He found an unknown mineral, heavy and black, looking very much like asphalt or coal. Arrhenius

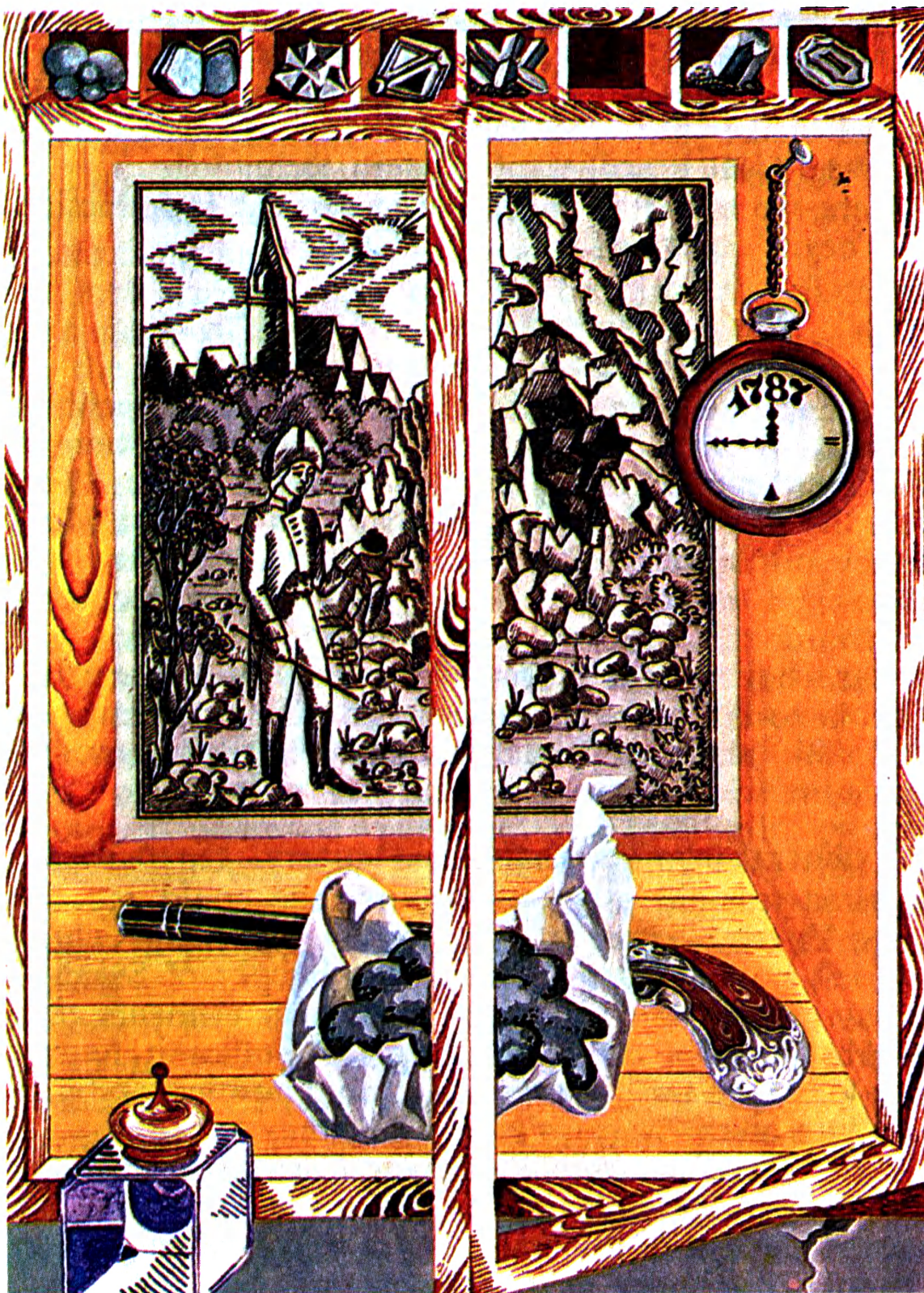


Fig. 1

did not know what the mineral consisted of; he just thought that it contained the recently discovered element tungsten. It did not take Arrhenius long to invent a name for the new mineral—let it be called ytterbite in the honour of the nearby village. At first it seemed just another new mineral, nothing special, only later generations could appreciate its real significance. As the mineralogist Flint wrote 130 years later, ytterbite was maybe the most significant single mineral in the history of inorganic chemistry.

Seven years later a specimen of ytterbite found its way to the laboratory of the professor of chemistry and mineralogy Johan Gadolin in the Finnish town of Abo (now Turku). The skilled experimenter isolated an oxide of an unknown element, a new “earth” from the specimen. Some time later the Swedish chemist Anders Ekeberg gave it the name “the yttrium earth” (after ytterbite and hence Ytterby). Thus, it is accepted that Gadolin discovered the first rare-earth element, yttrium, in 1794 and opened the history of rare earths.

But later it came out that what the professor from Abo had discovered was not a new chemical element but a complex mixture of the oxides of unknown rare-earth elements. So is it a mistake to claim that Gadolin discovered the element yttrium? In our opinion, it is. What we have here is a very peculiar case in the history of chemical elements in general. But traditions are not to be quarrelled with—let us stipulate that yttrium was discovered in 1794.

Leafing through the scientific journals of the end of the 18th century one can see how the name ytterbite disappeared and gave way to gadolinite suggested by Ekeberg (in honour of Gadolin). Further studies of gadolinite yielded substantially different results. All scientists who analyzed it reported varying contents

of yttrium in it—the Frenchman Louis Vauquelin reported a 35% content and the German Martin Klaproth a 60% content, though their analytical methods were identical.

A suggestion was made that gadolinite contained “something” unknown which was difficult to separate from the yttrium “earth” and hence the divergence in the results.

To sort out the situation chemists tried to find yttrium in other minerals. But not very many minerals were known to them at the time. However, one of them, known as “tungsten”, had baffled analytical chemists for quite some time. They thought it could contain some unknown substance.

One of the greatest chemists of all times, the Swede Baron Jöns Berzelius, took it upon him to find out the answer.

To look for India and find America. Berzelius and his teacher Wilhelm Hisinger performed a most careful analysis of a tungsten specimen. Contrary to their expectations, they did not find yttrium but still they discovered “something”. This “something” was in many respects similar to the yttrium “earth” but yet differed from it. This “something” became yellow upon heating and thus did not qualify as a classic “earth”.

In 1803 chemists could read a report by Berzelius and Hisinger about the discovery of “...a new and unknown substance. It has two types of oxides and gives rise to two kinds of salts—coloured and colourless... The substance is an oxide of the metal which we named cerium in honour of the planetoid Ceres discovered by the Italian astronomer Giuseppe Piazzi.”

But cerium repeated the history of yttrium—what was isolated by Berzelius and Hisinger was a complex

mixture of rare earths, rather than a single element. Thus, strictly speaking, 1803 as the date of the discovery is no more true than the date 1794.

What they found was something quite different from what they were seeking. The difference in the analysis results remained unexplained. Meanwhile, Klaproth independently isolated cerium from tungsten now renamed as cerite. Now nobody could question the existence of earthly namesake of the asteroid Ceres. Klaproth for a while claimed the priority of his discovery but having done some serious thinking was content to be honoured as a co-discoverer of the element.

The first decades of the nineteenth century, so slowly moving from the viewpoint of our rushed age, were full of brilliant achievements of science, including the discoveries of such major elements as sodium, potassium, boron, lithium, silicon, aluminium, thorium, vanadium, iodine and bromine. The rare-earth work looked rather boring in comparison and only a few scientists, not the least Berzelius, steadfastly continued it. Berzelius discovered several new rare-earth minerals and found that they often contained together yttrium and cerium (thus he partially solved the mystery of gadolinite). He developed procedures for separating yttrium and cerium (they came very handy later) and, finally, determined the atomic weights of the new elements and the formulas for the oxides YO and CeO and for the higher cerium oxide Ce_2O_3 . But he had also made a substantial error which brought much trouble to Mendeleev half a century later.

Berzelius had many students and some of them got interested in rare earths. One of them was the Swedish chemist Carl Mosander who suggested in 1826 that the cerium "earth" was not pure, that it, in its turn, also contained "something" else.

But it took chemists thirteen years to show that Mosander was right.

The “trees” start to grow. Mosander used to keep quiet about his ideas until he was completely sure of them and this time he was almost too late in making it public.

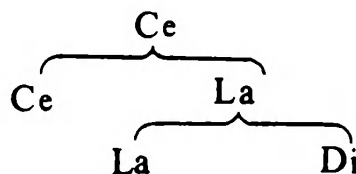
A Norwegian student of Berzelius, Axel Erdmann, found in February 1839 the long-expected “something” – an oxide of an unknown element – in the cerium “earth”. It was only when Berzelius told Mosander about that that the latter revealed that he had been studying the new “earth” for almost a year.

Berzelius suggested the name of lanthanum for the new-born rare-earth element (from the Greek for “escaping notice”).

Apart from the propensity for escaping notice, the new element had quite wayward ways. As it had earlier been the case with yttrium, lanthanum specimens obtained by different methods were different from one another in some hard-to-define ways. After two years of hard work Mosander was able to prove that the lanthanum oxide, in its turn, was not pure. It was contaminated with some unknown “earth”. Mosander named it didymium (from the Greek for “twin”). Indeed, lanthanum and didymium are bewilderingly similar.

These elements can be separated only after multiple recrystallization of their salts. Looking back, one can see it as a veritable chain reaction of discoveries – lanthanum isolated from cerium and didymium isolated from lanthanum and all three elements being strikingly alike.

Now Mosander could draw an impressive picture – a sort of a “rare-earth tree”:



The symbols for cerium (Ce) and lanthanum (La) can be found in the periodic table currently in use while the symbol for didymium (Di) cannot. Just note this fact for the time being.

Of course, there was also yttrium. Now Mosander started working on and in 1843 the tenacious chemist managed to split yttrium into three components—yttrium proper (Y), erbium (Er) and terbium (Tb)—something that nobody succeeded in doing since the first attempts of Vauquelin and Klaproth. The last two names also originated from the name of that small village in Sweden.

This is how the second (yttrium) “rare-earth tree” looked like:



But nobody, including Mosander, could be sure that all the known six rare-earth elements were not a mixture.

But chemists could not prove it for almost forty years. The rare earths are too much alike. It is extremely difficult to separate them from one another and there are no reliable methods to control their separation.

Thus, what chemists had to do first was to study in detail the properties of the rare earths and to develop new analytical techniques.

Mendeleev and rare earths. On March 1, 1869 Dmitri Mendeleev sent to many Russian and foreign scientists

a small table entitled *A system of elements based on their atomic weights and chemical similarity* (Fig. 2).

It was yet an early prototype of the future periodic system. Mendeleev still had not a clear understanding of periods and had not fully made up the groups of similar elements. He had to banish some elements to the bottom of the table, to its periphery. They included the rare-earth elements yttrium, cerium, lanthanum, didymium and erbium. The Russian chemist had doubts about the existence of terbium.

Soon after that he wrote in his first paper on the periodic law that the rare-earth elements were “outside the system for the time being”. He was quite justified in writing this—too little was known about these elements and what was known raised certain questions.

For instance, following the authoritative opinion of Berzelius, many chemists thought that rare-earth elements were divalent and wrote the formulas for their oxides as MeO and for cerium also as Me_2O_3 (here Me is a metal). But were they right?

The elements had such atomic weights:

Y	La	Ce	Di	Er
60	94	92	95	56

But who could be sure that the weights had been determined accurately?

When Mendeleev started working on the periodic system he had to make do with these data.

Having thought over the properties of rare earths he decided that they were not chemical analogues of magnesium and calcium. That meant that they had no place in the second group of the periodic table which contained divalent elements. In fact, this group had no free room for them.

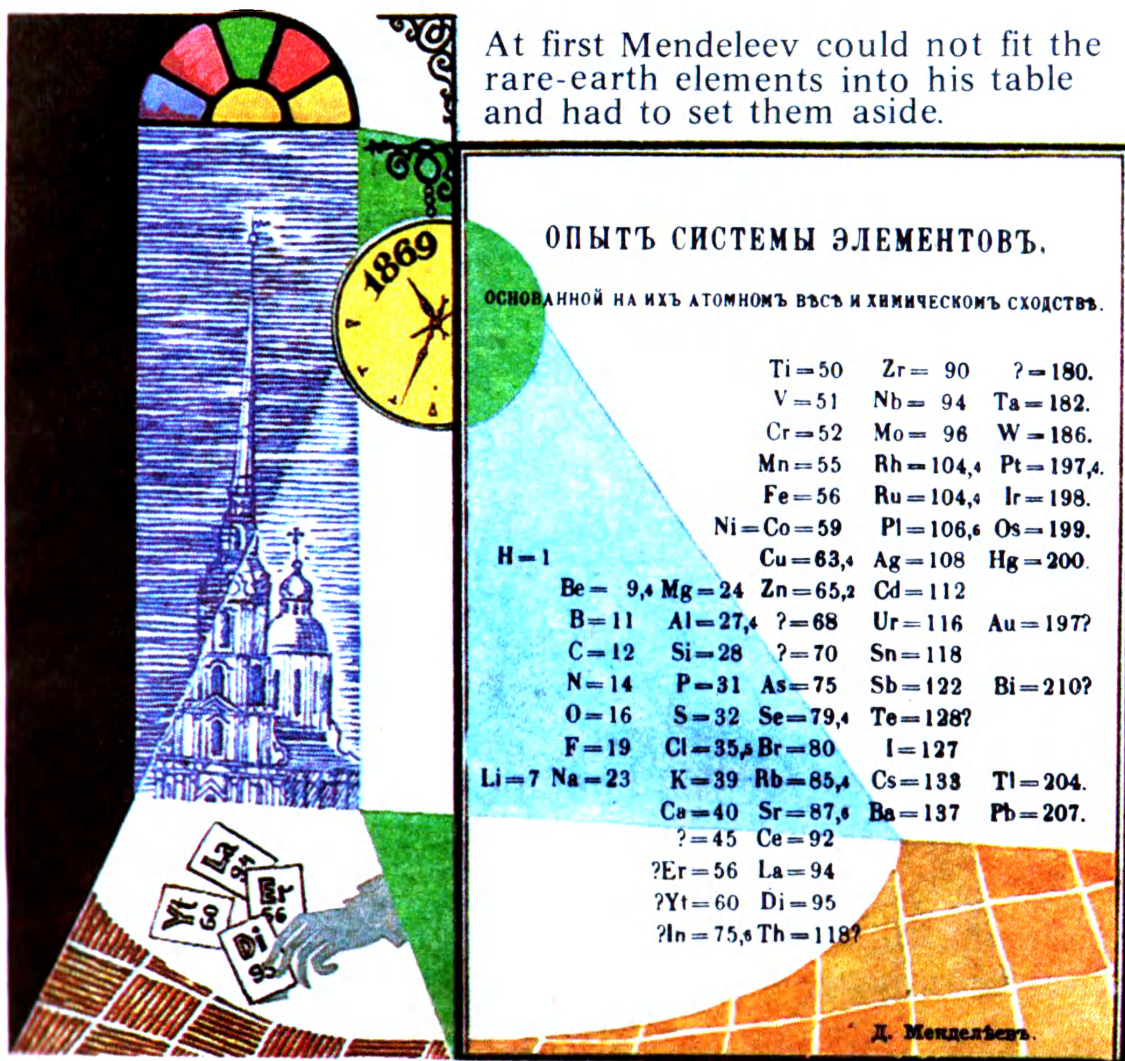


Fig. 2

Mendeleev then thought that maybe rare-earth elements were in fact trivalent and had to be assigned to the third group which had suitable vacancies. But the implication was that Berzelius was wrong and the formula of the rare-earth oxides had to be written as Me_2O_3 . The formula of the oxide of cerium which in all probability had also the valence of four had to be written as CeO_2 . But the placement of the rare-earth elements to the third group could be given a serious consideration only under the assumption that their atomic weights were much higher.

Mendeleev made a bold decision to increase their atomic weights by approximately fifty percent. It was the first instance when the periodic system suggested reconsideration of atomic weights, and it was perhaps the first practical application of the periodic law.

Such were the new atomic weights:

Y	La	Ce	Di	Er
88	138	139	140	175

Now yttrium could be easily accommodated in the fifth period of the system between strontium and zirconium:

Sr	Y	Zr
87	88	90

A new place for lanthanum was also easily found in the sixth period after barium:

Ba	La
137	138

But cerium proved to be harder to place. Its atomic weight was such that it could not be put into the third group as an analogue of lanthanum. However, a solution of sorts was suggested. Since cerium could have a valence of four it could be put into the fourth group under zirconium.

One could think that this solution would greatly simplify the situation. But who could be sure that the atomic weight of cerium was indeed such as suggested by Mendeleev? So far, it was just a bold hypothesis. What next?

Erbium was the heaviest of the rare-earth elements. Its atomic weight was such that it could tentatively be placed under lanthanum, that is, in the seventh

period. But it was nothing more than a subterfuge, particularly so as the properties of erbium were practically unknown.

As for didymium, nothing at all could be done about it. It could not be assigned either to the third or to the fourth group. Perhaps it could be assumed to have the valence of five? An extremely doubtful assumption.... Maybe its atomic weight was much higher?

Mendeleev clearly knew that the rare-earth elements would give rise to numerous complications for his periodic system. He tried one by one various ways for arranging them. Here is the arrangement he tried in 1871:

Y	89		
La	139	Ce	140
Er	170	Di	175-180

In the arrangement of 1873 he changed the positions of didymium and lanthanum and the atomic weights:

Y	88		
Di	138	Ce	140 (138?)
Er	178	La	180

Here is another arrangement tried by Mendeleev in 1877:

Y	88			
La	138	Ce	139	Di? 142?
Er	175	?		

The question marks reflect Mendeleev's lack of confidence, it was painful for him but he could not find a clear-cut solution which would remove all doubts.

Not long before Mendeleev's death when the problem of rare earths was understood better he wrote bitterly

about his attempts to place them in the periodic system: "...I have not yet made any decision and I see it as one of the major difficulties produced by the periodic system." He wrote that in 1906.

Thirty years later the German chemist Walter Noddack, a well-known expert on rare earths, said: "Each time somebody suggests his version of the periodic system he suggests a different arrangement of the rare-earth elements in it."

But the difficulties encountered by the periodic system in the seventies of the last century could give only a weak foretaste of much greater troubles that lay ahead.

The only consolation was that the number of the rare-earth elements was rather small—just six. Thirty years had passed since Mosander's discovery and their number remained unaltered.

But this seeming lull had to end.

Horn of plenty. Why did it take so long to discover new rare-earth elements?

Because too few minerals containing rare earths were known. Gadolinite and cerite, these old workhorses, were very rare while the other such minerals (fewer than ten of them) were so uncommon as to be virtually museum pieces.

A new mineral discovered in the USA in 1878 attracted much attention. It was named samarskite. This Russian-sounding name was given to the mineral because it proved to be identical to an unknown mineral found by the Russian mining engineer V. Samarsky in the Ural mountains in the middle of the sixties.

It was later that everybody understood that samarskite was a veritable "store" of rare-earth elements. However, "shopping" in it did not come easy at first.

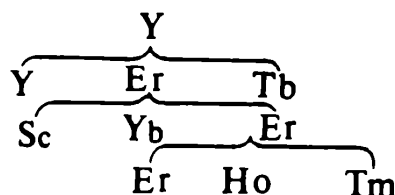
Five new rare earths were claimed to be discovered in 1878 and all these discoveries were based on experimental errors.

There was only one success—the Swiss chemist Jean de Marignac proved that erbium extracted from good old gadolinite contained an impurity. Marignac worked hard on separating the impurity from erbium and claimed the discovery of a new element. It happened on October 22, 1878. The name of the new element—ytterbium—also was rooted in the name of that famous village—Ytterby.

The prominent Swedish chemist Lars Nilson made the discovery of the next year, 1879. He analyzed Marignac's ytterbium and found a new element, scandium, in it. Moreover, it was not just another new element, it was Mendeleev's "eka-boron". That was an unknown element predicted by Mendeleev in 1870 which had to be a chemical analogue of boron and be placed in the fourth period of the periodic system between calcium and titanium. That was one of the few cases when newly found rare-earth element was immediately placed in the periodic system. Thus, "eka-boron" gave way to scandium (for Scandinavia).

Another Swede, Per Clève, who was a no less prominent chemist than Nilson, decided "to put on trial" the erbium that remained after separation of ytterbium and scandium from it. It came out that the "pure" erbium contained in fact three components—erbium proper and two new rare-earth elements, holmium and thulium. Holmium was named after the ancient Latin name *Holmia* for the Swedish capital Stockholm. Thulium received its name from the Latin name *Thule* for the northernmost part of the ancient habitable world. Clève was implying by this name that to obtain thulium was as difficult as to reach the northern boundary of the world.

Now look at the lush growth of the yttrium “tree” of rare earths in just two years:



Soon it was the cerium “tree” that brought forth surprising branches.

First it was tended by the French chemist Paul de Boisbaudran (who in 1875 discovered the first of the elements predicted by Mendeleev – gallium).

Boisbaudran analyzed didymium extracted from samarskite. Now it was the turn of Mosander’s didymium to fail the test of time. On July 16, 1879 the French chemist announced his discovery of samarium (the origin of the name is clear).

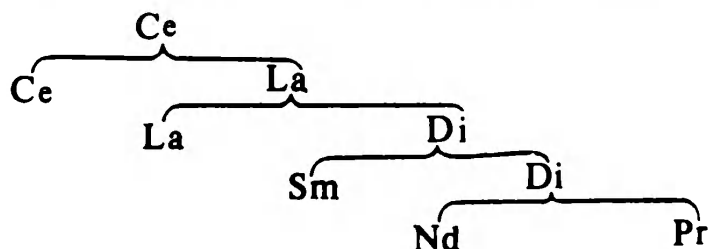
Six years later the Austrian chemist Carl Auer von Welsbach emerges as a new hero on the scene. He had made an invaluable service to the studies of rare earths by attracting the attention of industry to them. At the time the prevalent form of illumination in the world was gas lighting. In 1884 von Welsbach invented a gas mantle of incandescent character which was impregnated with thoria and rare earths, had a longer service life and provided for higher luminosity.

The invention stimulated a search for new rare-earth deposits and it was successful. In 1886 extensive deposits of the so-called monazite sand were found in Brazil. This sand had a high content of rare earths and the demand of chemical laboratories for rare-earth specimens was at long last satisfied.

It was von Welsbach who crossed out the name didymium and the symbol Di from the list of chemical elements. He reported to a meeting of the Viennese

Academy of Sciences on June 18, 1885 that he had split didymium into praseodymium (the “green twin” from the green colour of the solutions of its salts) and neodymium (“new twin”). This was the only instance in the history of rare earths that the name of a mixture of rare earths was not fully retained in the name of one of the components.

After that the cerium “tree” had the following shape:



We see that on this “tree” only cerium found early by Mosander has not produced any new “branches”, that is, new rare-earth elements.

A year later, in 1886, each tree gave forth a new branch—Marignac separated dysprosium (from the Greek for “hard to get at”) from holmium in the yttrium “tree” and Boisbaudran discovered gadolinium (for Gadolin) in samarium in the cerium “tree”.

The name dysprosium gives an apt description of the story behind the discoveries of rare-earth elements. The bare dates of discoveries and the ordered-looking “trees” do not reveal the hard work of the chemists, the doubts they had at each step. There is a thick tangle of false discoveries around each “tree”, like a tangle of vines in jungle. The price of truth was indeed high.

Why was it so high?

A necessary explanation. As new and new rare earths were discovered scientists grew increasingly aware of a

The prominent German scientists Robert Bunsen and Gustave-Robert Kirchhoff invented the method of spectral analysis in 1860. It stemmed from the discovery that when a grain of a substance was placed into the flame of a burner the spectrum of the emitted light was peculiar to the elements in this substance.

It became possible to find out definitely whether a given chemical element was present in a substance by analyzing the spectrum of the substance, that is, the arrangement of the spectral lines in it.

But spectral analysis proved to be a mixed blessing for the study of rare earths. Now we know that the optical spectra of rare-earth elements are highly complicated and contain many lines. Even now it is not easy to interpret these spectra. It was much more difficult at the end of the last century when the scientists knew nothing about the atomic structure and no spectroscopic theory existed.

It is no wonder then that spectral analysis gave rise to many mistakes when it was applied to rare-earth elements. It was not all bad, though spectral analysis contributed to the discoveries of holmium, gadolinium and dysprosium.

But in many instances it was a source of great confusion.

The drowned truth. Historians of chemistry say that in the 35 years from 1878 to 1913 the discoveries of at least 100 new rare-earth elements were reported in scientific journals. Only 13 of them were real discoveries. Apart from those discussed above, there were other two definite discoveries—europium in the cerium “tree” and lutetium in the yttrium “tree”. The first discovery was made by the French spectroscopist Eugène Demarcay (one of the cases when spectral analysis helped) in 1901 and the second was made by

Urbain in 1907. Demarcay's element was the first discovered in the 20th century, he called it europium (in honour of Europe) while Urbain gave his element the name of lutetium (after the ancient Latin name of Paris – Lutetia).

Lutetium was later found to close the rare-earth series. But this is a different story and we shall tell it later.

All other reported discoveries were mistakes. Here are several such stories of error.

Immediately holmium and dysprosium had been discovered the Swedish chemist Lars Nilson and his co-worker Hermann Kruss made a sensational claim – holmium could be divided into four components and dysprosium into three components. Then they found at least eight components in neodymium and praseodymium. Luckily for them, they were tactful enough not to give immediately names to the newly discovered elements. Meanwhile, grand-sounding names of new elements frequently appeared in scientific journals – austrium and russium, demonium and damarium, decipium and lucium. We shall not present here the names of the unfortunate “discoverers” who were too rash in announcing their discoveries. There was one Kosmann, though, who reported a discovery of kosmium and neokosmium as a practical joke on the April Fools' Day – one of the lighter pages in the history of rare earths.

Practically each year several new “rare-earth meteors” briefly flashed across the skies of chemistry. Often errors were immediately revealed but sometimes it was sooner said than done. One could not help wondering if there could be an end to all of it. Was the number of the rare-earth elements limited?

This suggestion could be alarming or even dangerous for the periodic system. One recalls how frustrating

phenomenon never before encountered in chemistry. It was an amazing chemical similarity of rare-earth elements—all of them were typically trivalent and entered the same chemical reactions. That was why they were found together in nature.

Though their properties are similar, they nevertheless are not identical. There are certain differences and a skillful use of them makes it possible to separate what seems inseparable. Their salts, for instance, nitrates, have different solubilities. The solubility decreases with increasing atomic weight of the elements. Though the decrease is small, it can help the chemist when properly employed. This separation method is known as the fractional crystallization.

This is what the chemist had to do. After preparation of a solution of rare-earth nitrates he evaporated it and left for crystallization. The less soluble salts were the first to appear in the sediment, and the more soluble salts remained in the solution. The solution was filtered, diluted, evaporated and crystallization was repeated. The first portion of crystals was dissolved, the solution was evaporated, sediment was removed and the procedure was repeated in the same order. The technique of fractional crystallization is schematically illustrated in Fig. 3.

Other methods were also employed but the above illustration is enough to show how arduous and monotonous the work on separation of rare earths was. To obtain *relatively* (just relatively!) pure specimens the procedure had to be repeated many hundreds or even thousands of times. To extract a more or less pure thulium Urbain in his time had to perform more than 10 000 recrystallizations.

Such was the price of truth.

What is described above was only a part of work. The separation processes had to be controlled with

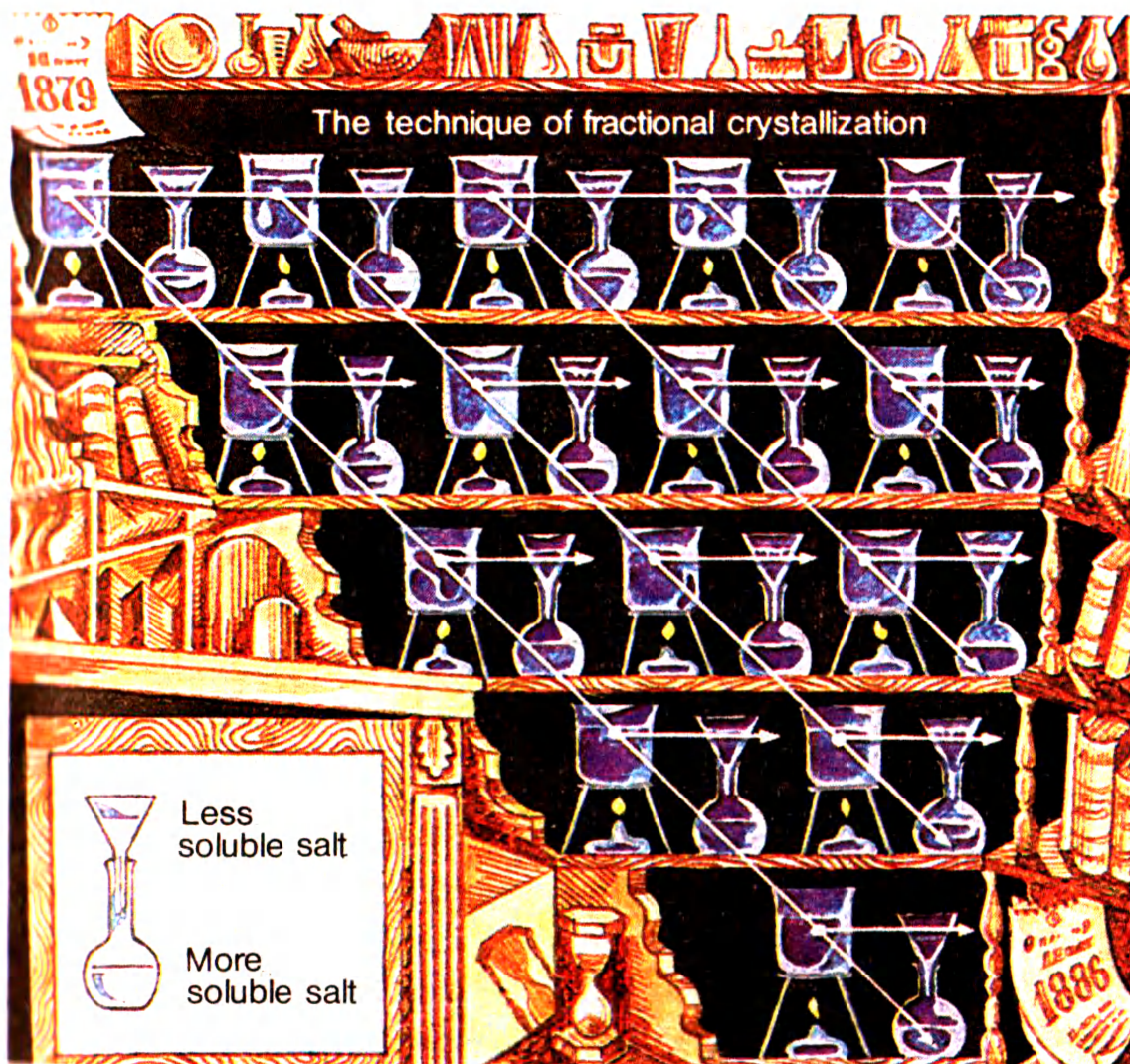


Fig. 3

some rigorous and reliable methods. Chemists had only one method of control—to measure from time to time the molecular weights of the obtained fractions. If the molecular weight remained more or less constant that meant that separation was practically completed and a “pure” preparation of a certain rare earth was extracted. But the method used for determination of the molecular weight was so tricky and cumbersome that it is not accidental that we put the word pure above in inverted commas.

The physical method of control seemed more reliable.

The prominent German scientists Robert Bunsen and Gustave-Robert Kirchhoff invented the method of spectral analysis in 1860. It stemmed from the discovery that when a grain of a substance was placed into the flame of a burner the spectrum of the emitted light was peculiar to the elements in this substance.

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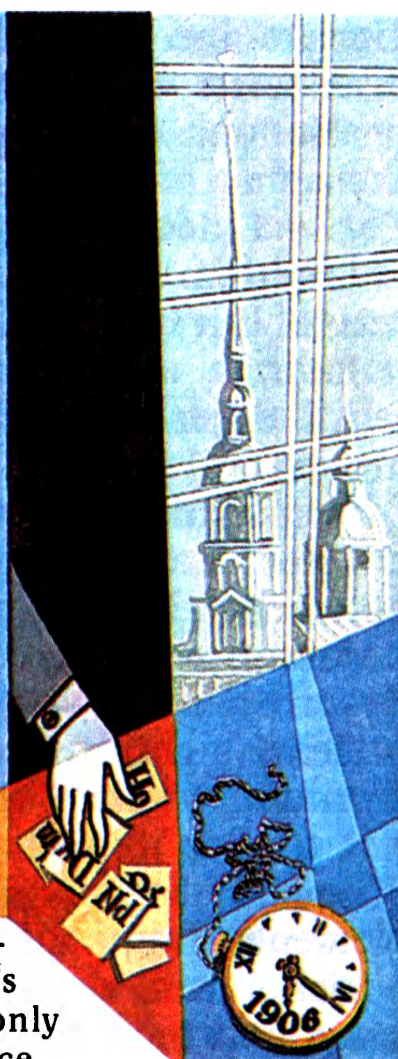
All other reported discoveries were mistakes. Here are several such stories of error.

Immediately holmium and dysprosium had been discovered the Swedish chemist Lars Nilson and his co-worker Hermann Kruss made a sensational claim – holmium could be divided into four components and dysprosium into three components. Then they found at least eight components in neodymium and praseodymium. Luckily for them, they were tactful enough not to give immediately names to the newly discovered elements. Meanwhile, grand-sounding names of new elements frequently appeared in scientific journals – austrium and russium, demonium and damarium, decipium and lucium. We shall not present here the names of the unfortunate “discoverers” who were too rash in announcing their discoveries. There was one Kosmann, though, who reported a discovery of kosmium and neokosmium as a practical joke on the April Fools' Day – one of the lighter pages in the history of rare earths.

Practically each year several new “rare-earth meteors” briefly flashed across the skies of chemistry. Often errors were immediately revealed but sometimes it was sooner said than done. One could not help wondering if there could be an end to all of it. Was the number of the rare-earth elements limited?

This suggestion could be alarming or even dangerous for the periodic system. One recalls how frustrating

4	Ар- гонъ. Ar 38	Ка- лий. K 39,15	Каль- ций. Ca 40,1	Скан- дий. Sc 44,1	Ти- танъ. Ti 48,1	Вана- дій. V 51,2	Хромъ. Cr 52,1
5		Мѣдъ. Cu 63,6	Цинкъ. Zn 65,4	Гал- лій. Ga 70,0	Гер- маній. Ge 72,5	Мышь- якъ. As 75	Се- лень. Se 79,2
6	Крип- тонъ. Kr 81,8	Ру- бидій. Rb 85,5	Строн- цій. Sr 87,6	Ит- трій. Y 89,0	Цир- коній. Zr 90,6	Ніо- бій. Nb 94,0	Молиб- денъ. Mo 96,0
7		Сере- бро. Ag 107,93	Кад- мій. Cd 112,4	Ин- дій. In 115,0	Оло- во. Sn 118,0	Сурь- ма. Sb 120,2	Тел- луръ. Te 127
8	Ксе- нонъ. Xe 128	Це- зий. Cs 132,9	Ба- рий. Ba 137,4	Лан- танъ. La 138,9	Це- рій. Ce 140,2	—	—
9		—	—	—	—	—	—
10	—	—	—	Иттер- бій. Yb 173	—	Тан- талъ. Ta 183	Вольф- рамъ. W 184
11		Зо- лото. Au 197,2	Ртуть. Hg 200,0	Талій. Tl 204,1	Сви- нецъ. Pb 206,9	Вис- мутъ. Bi 208,5	—
12	—	—	Радій. Ra 225	—	Торій. Th 232,5	—	Уранъ. U 238,5



A fragment from the periodic table published in the eighth edition of Mendeleev's *Fundamentals of Chemistry* (1906). The only rare-earth elements about whose existence Mendeleev had no doubts were Sc, Y, La, Ce and Yb.

Fig. 4

it was for Mendeleev to fit just five rare-earth elements into the periodic table. And by the end of the eighties there had been almost a dozen of them and even if one did not wholly believe in the existence of all of them one had to reckon with them. All of them were so similar to one another that it went without saying that they could not be allocated a slot each in various groups of the periodic system. Mendeleev dealt with them extremely cautiously. In the tables given in the

successive editions of his *Fundamentals of Chemistry* one sees only blank spaces between cerium and tantalum.

Nobody could say how many rare-earth elements existed in nature. Some chemists tried to explain the close similarity of their properties. Maybe, the similarity of atomic weights was the reason? But the difference between the atomic weights of neodymium and samarium was as large as six units. Apparently, there was a different reason.

Now a new character appears in our story—the outstanding English scientist Sir William Crookes. Crookes put forward an unusual hypothesis to account for the nature of the rare-earth elements. He believed they were essentially different from the conventional elements. In his opinion they were something like modifications of one or several elements which he called metaelements. Crookes tried to substantiate his idea with spectral observations.

If Crookes' hypothesis had been proved the terrifying abundance of the rare-earth elements would have ceased to be a mystery. But the spectral analysis once more proved to be "uncooperative" and other scientists demonstrated the mistake of the English scientist.

The hypothesis of metaelements collapsed but it often happens that even erroneous ideas contain a grain of truth. When Crookes suggested that conventional elements were a mixture of metaelements he in fact assumed that each element consisted of different atomic species. He even suggested replacing the concept of the element with the concept of the elementary group. Now that we know that many elements are natural mixtures of isotopes we cannot help being amazed with this prediction of Crookes that he had made almost 30 years before the discovery of isotopism.

Despite this cheering example, we must admit that

rare earths constituted a major problem of inorganic chemistry and caused great trouble for the periodic system at the end of the last century.

In anticipation of great events. But chemists worked on and on dredging the “sea of errors” for grains of truth and gradually, often intuitively, obtained more or less definite results.

Their strenuous efforts were bearing fruit. Some of the reported discoveries of the rare-earth elements were confirmed, others remained as curiosities in the history

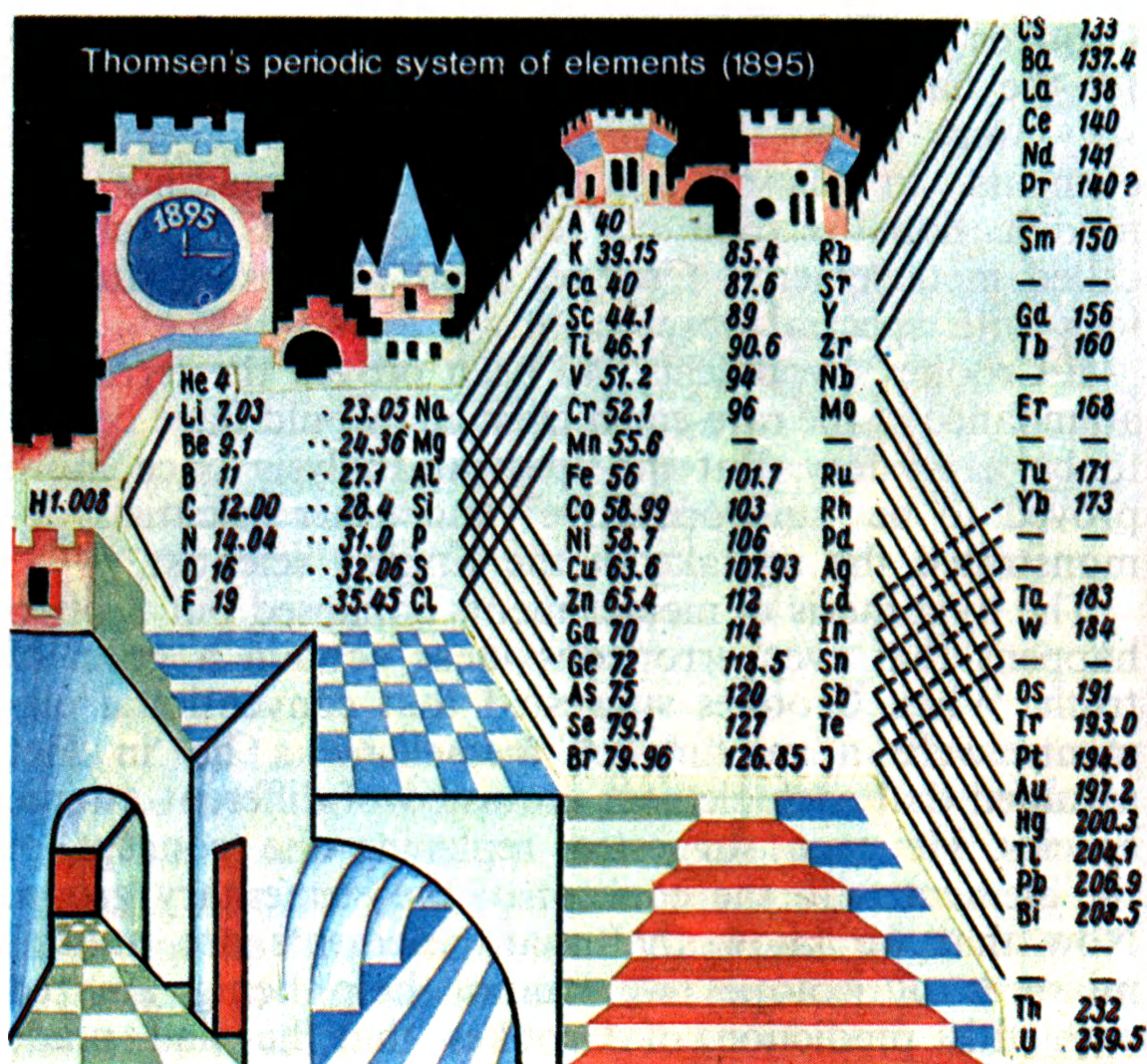


Fig. 5

of chemistry. The gas lamps with incandescent Welsbach mantles gave way to electrical lighting in cities. There was plenty of raw material for extracting rare earths—the monazite sand which had formerly been used as ballast for homeward-bound ships from India. This ballast now served the science of chemistry.

The “trouble-free” rare-earth elements, scandium and yttrium, occupied now a somewhat privileged position—they had assured slots in the periodic table. However, nobody, of course, could be sure that they were completely pure and had no admixtures. Anyway, chemists focussed their attention on the interval between barium and tantalum.

The Danish chemist Julius Thomsen put forward his own graphical representation of the periodic system in 1895. It was a prototype of the modern ladder-type table of elements. Note how original and symmetric its structure is (Fig. 5). One feature of it is that it limits the number of possible rare-earth elements. The dashes show the positions of the rare-earth elements unknown to Thomsen. The position between Sm and Gd was filled by europium in 1901 and the position after ytterbium was filled by lutetium in 1907. The dashes between Tb and Er and between Er and Tm corresponded to dysprosium and holmium which had already been known at the time and it is unclear why Thomsen ignored these elements.

The important thing is that Thomsen believed that only 15 elements—no more, no less—had to appear in the table between barium and the “yet unknown element with the atomic weight of 181”.

Thomsen was exactly right, though he could not give any proof of his opinions. The only support he could get was from the very structure of his table which seemed to determine the number of rare-earth elements.

The Czech chemist Bohuslav Brauner, a friend and follower of Mendeleev's, was perhaps the most prominent of the chemists studying rare earths. Brauner was active in the field for a quarter of a century. He had made more precise determination of the atomic weights for many rare-earth elements and had been close to finding the components of didymium. It was just his bad luck that von Welsbach was the first to do that. His another important achievement was his confident prediction that the rare-earth series contained an unknown element between neodymium and samarium. There is a special chapter in this book describing it.

In short, Brauner was rightly thought to be one of the most experienced workers in the field. It is not surprising therefore that it was he who found a highly imaginative way to arrange the rare-earth elements in the periodic table.

He described it for the first time at a congress of Russian natural scientists and physicians in Saint Petersburg on December 21, 1901.

Brauner's idea consisted in the following:

"As in the solar system a whole group of asteroids occupies a belt along the path where, by analogy, a single planet would be travelling, a whole group of the rare-earth elements could occupy a position in the periodic system which otherwise would belong to a single element...." Brauner named the rare-earth series the interperiodic group and regarded it as a continuation of the fourth group.

Talking in the modern language we would say that what Brauner actually suggested was to place the rare-earth elements into the cerium slot. This approach eliminated the need to search for a place for each rare-earth element in the table and was fully consistent with their amazing chemical similarity (Fig. 6).

Placement of the rare-earth elements in the periodic system according to Brauner (1902)

	I ^o	II	III	IV ^o	V	VI	VII	VIII	0
7	Ag	Cd	Jn	Sn	Sb	Te	J		Xe
8	Cs 133	Ba 137	La 139	Ce 140 Pr 141 Nd 144 — Sm 148 Eu 151 — Gd 156 — Tb 163 Ho 165 Er 166 — Tm 171 Yb 173 ? 180					
9	Au	Hg	Tl	Pb	Bi	—	—	—	—
10	—	Ra	—	Th	—	U	—	—	—

Fig. 6

Brauner's contemporaries were not impressed with his idea. The only response was Mendeleev's cautious remark that "it deserved greater attention". This coolness apparently discouraged Brauner and for a time he even retracted his suggestion which was in principle correct.

The German chemist Richard Meyer took up Brauner's idea in 1913. He made a significant modification, though—he suggested placing all the rare-earth elements into the third group and putting the entire series from lanthanum to lutetium into the lanthanum slot.

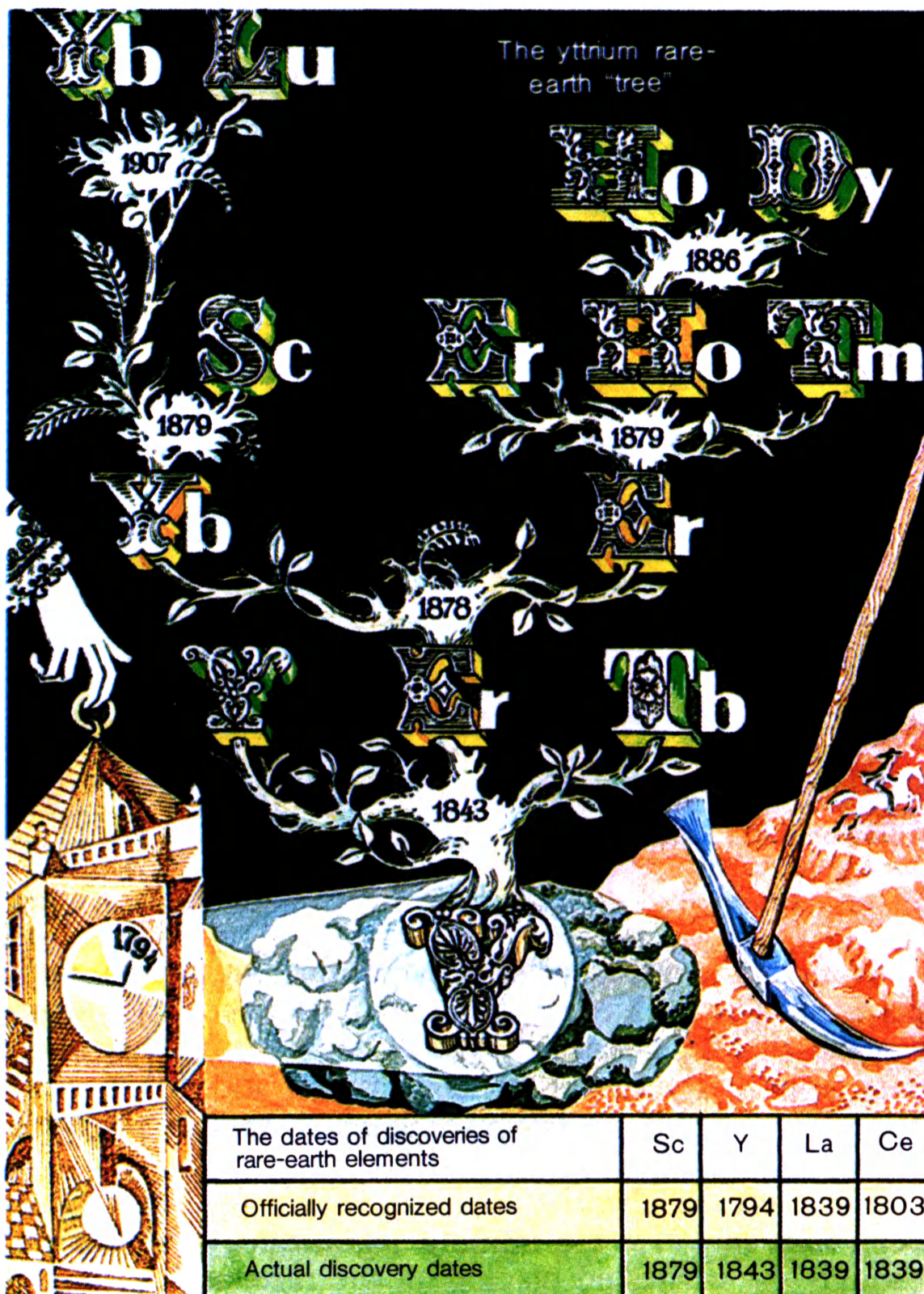
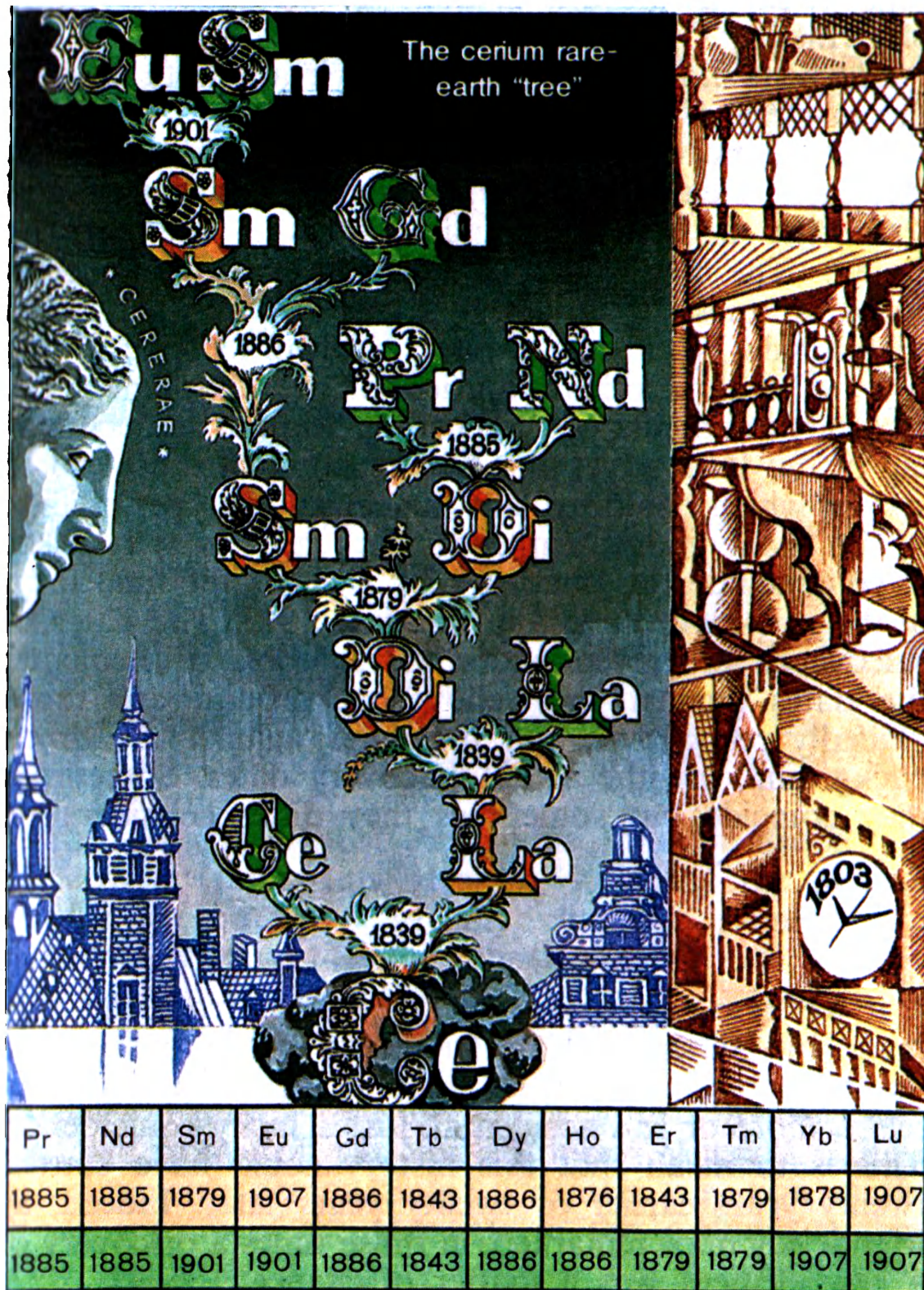


Fig. 7



This is exactly how it is done in the modern tables of elements.

Chemists did all they could in their attempts to solve the mystery of rare earths.

They tentatively determined the total number of the rare-earth elements and suggested a convenient and consistent method of arranging them in the periodic system. The truth was somewhere near, its outlines could be guessed but all this was a purely empirical achievement, a result of practical work. Theory was lagging behind. A real solution of the problem of the rare-earth elements was impossible without understanding of the laws governing the structure of the periodic system which could explain the cause of its periodicity.

The final judgement was the task of physicists.

To conclude this chapter Fig. 7 shows the final form of the rare-earth “trees” in the year 1913. The dates of discoveries are given under the symbols of elements; the dates against the yellow background are those officially recognized, and the dates against the green background are the actual discovery dates. Sometimes they coincide but sometimes they differ considerably.

The Birth of Truth

If we date the history of rare earths from the find made by lieutenant Carl Arrhenius or from the year when Gadolin isolated the yttrium “earth” its beginning seems more or less accidental, just a lucky coincidence. This is to mean that this history could have started twenty years earlier or twenty years later. Indeed, as Mendeleev once remarked, in those times a discovery of a new element was a matter of chance.

Early in the 20th century the work on rare earths was not such a “chancy business”. But even the most

skilled chemists well-versed in the “rare-earth lore” would not have dared to state that no new element could be added to the series between cerium and tantalum. The prominent English scientist George Spencer published a fundamental monograph *The Rare-Earth Elements* in 1911 where he seriously declared that erbium, dysprosium, holmium, thulium and cerium were yet to be split into other elements.

But it happened that physics became involved in the fate of the periodic law—it was an inevitable result of science development and it was physics that brought out the ultimate truth from the “sea of errors”.

Moseley’s law. The English physicist Henry Moseley did not live long—in the prime of life he was killed by a stray bullet in the First World War.

But he did very much for science in just five-six years of his research career.

He erected a physical foundation under the Mendeleev law and did it not with abstract theory but with rigorous experiments.

The Dutch scientist Antonium Van-den-Brook put forward an interesting idea in 1913 that the nuclear charge in the atom of any chemical element was numerically equal to its number in the periodic system. If somebody had proved this idea many problems of the periodic system would have been solved.

It was precisely such a proof that was found by Moseley. He measured the wavelengths of X-rays emitted by atoms of various chemical elements. These measurements demonstrated a regular variation of the X-ray spectra of the elements in the periodic system. This regularity is clearly seen in Fig. 8 which schematically shows the lines in the X-ray spectra of the elements from titanium to copper. The law found by Moseley states that the square root of the frequency

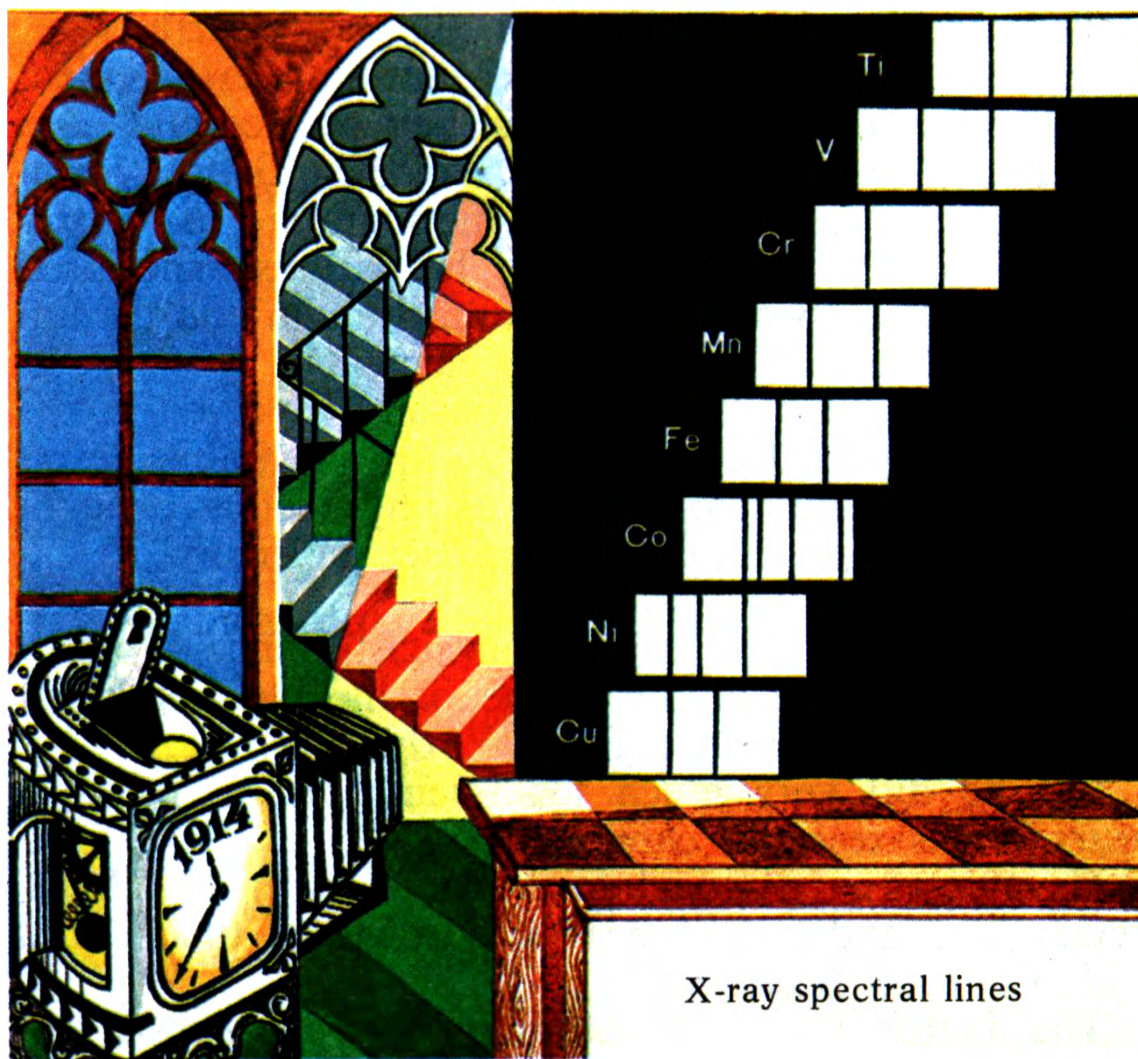


Fig. 8

of a spectral line is proportional to a quantity which changes by unity and proves to be the difference between the atomic number of the element and a constant.

What were the implications of Moseley's law? It indicated that there had to be 92 chemical elements—no more, no less—within the periodic system between hydrogen and uranium.

It identified the slots of the periodic table which had to contain the yet undiscovered elements with the atomic numbers 43, 61, 72, 75, 85, 87 and 91.

It confirmed the order of elements in the rare-earth series established empirically by chemist which started with lanthanum (No. 57) and ended with....

It is not accidental that we did not finish the above sentence. Even Moseley's law could not predict the number of the last rare-earth element. The seventy-first element, lutetium, had already been found but the element No. 72 had not been discovered yet. It could either be the last rare-earth element or an analogue of zirconium, that is, be outside the rare-earth series.

Thus, the next thing to find out about rare-earth elements was their total number; it could be 15 or 16 (in both cases we take into account the unknown element No. 61).

A small but important digression. The chemist Urbain and von Welsbach again appear in these pages. We have mentioned above that in 1907 Urbain managed to split ytterbium into two components to one of which he gave the old name of ytterbium and to the other the name of lutetium.

But von Welsbach did the same independently of Urbain. He gave the fine-sounding names of aldebaranium and cassiopeium (for the well-known constellations) to the "newly discovered" elements. Soon the name aldebaranium gave way to ytterbium but von Welsbach did not give up his claim on the discovery of one new rare-earth element which he named cassiopeium. In fact, he reported his discovery only a short time after Urbain had done it.

In principle, it is not important how we call the new element—lutetium or cassiopeium—it is the discovery itself that matters. Though most scientists recognized priority of Urbain's claim the symbol Cp for cassiopeium was retained for a relatively long time in German literature.

(In fact, the European scientists just missed having a strong overseas competitor. Before the news about the discoveries of lutetium and cassiopeium reached American shores Charles James from the University of New Hampshire (USA) had obtained a large amount of the oxide of the element No. 71. But James did not even try to claim his priority, either because of his extraordinary modesty or for some other reasons, thus depriving New World of a rare chance to give birth to a new element, especially rare as all the elements before that had been discovered by Europeans.)

Urbain was greatly encouraged with his success and once again decided to try his luck. He carefully performed recrystallization of lutetium salts and produced what he thought was a new rare-earth element with the atomic weight greater than that of lutetium. Urbain gave this element the name of celtium.

When Moseley irrefutably demonstrated that there had to be an unknown element between lutetium and tantalum Urbain immediately responded that celtium was the element No. 72 and the last element in the rare-earth series.

Urbain stubbornly continued to defend his view, though Moseley had shown in experiments that the very existence of celtium was questionable.

At the very beginning of 1923 the scientific community was stirred by the significant piece of news—the Hungarian radiochemist George de Hevesy and the Danish spectroscopist Dirk Coster found the element No. 72 in the zirconium ore from Norway. Its properties were very close to those of zirconium and that meant that it did not belong to the rare-earth series.

But the especially significant thing about that discovery was that even before conducting their experiments Hevesy and Coster had been sure that the element No. 72 would be a chemical analogue of zirconium.



Fig. 9

Their belief was based on the scientific theory describing the structure of atoms of chemical elements; the foundations of this theory had been developed by the great Danish physicist Niels Bohr.

This element was named hafnium (after the ancient name Hafnia for Copenhagen). Now the problem was to choose between hafnium and celtium.

The solution of this problem had many important implications. It could pass the final judgement about the number of the rare-earth elements in the periodic table. But there was something else, too.

What is the structure of the atom? If hafnium was the element No. 72 that meant that the atom of this element had the structure predicted by Bohr.

Back in 1911 the British physicist Sir Ernest Rutherford suggested that the atom could be regarded as something like a small-scale model of the solar system. At the centre of it was the positively charged massive nucleus (Sun) with electrons (planets) rotating about it in their orbits. Rutherford's model of the atom became known as the planetary or nuclear model.

Bohr modified this model assuming that electrons rotated in chosen, rather than any possible, orbits. Close electron orbits were grouped into electron shells denoted by the letters *K*, *L*, *M*, *N*, *O*, *P* and *Q* which were at different distances from the nucleus. The *K* shell was the closest to the nucleus, the next was the *L* shell and so on.

Each shell had to contain a finite number of electrons. Bohr denoted each shell by the number n and demonstrated that the largest number of electrons in an electron shell was $2n^2$.

The table below illustrates it.

	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>	<i>O</i>	<i>P</i>	<i>Q</i>
n	1	2	3	4	5	6	7
$2n^2$	2	8	18	32	50	72	98

Another significant feature of Bohr's model was that each electron shell consisted of subshells. Each subshell had to contain a definite number of electrons but Bohr did not know yet how to determine this number.

But even this knowledge about the structure of atoms helped Bohr in his attempts to relate the properties of elements to their atomic structure. This implied looking for the causes of periodic variation of

the properties of chemical elements, that is, developing a theory of the periodic system.

Later we shall tell in this book how this theory took finally the truth out of the "sea of errors", explained why the rare-earth elements were so similar in their properties and determined their real number. Now, let us continue with the following question:

What is the main structural feature of the periodic system? Maybe, it is the fact that the periodic system reflects the periodic law according to which the properties of chemical elements vary periodically with increasing atomic number Z ? Or is it the fact that chemically similar elements belong to certain groups?

For instance, oxygen, sulphur, selenium, tellurium and polonium belong to the sixth group of the periodic system. But this group contains a parallel column of three more elements—chromium, molybdenum and tungsten. They are also similar to one another. Both these series of elements are in the same group. Each group of the periodic system is further divided into two categories—the main group (A) and the subgroup (B). In the sixth group discussed above oxygen and its analogues make up the main group (A) and chromium and its analogues make up the subgroup (B).

But still it is not the most significant structural feature of the periodic system.

Now assume that the most fundamental thing about the periodic system is the concept of the period. Indeed, Mendeleev's system is known as the periodic system because it consists of several periods. Each period contains a certain number of elements. Each period starts with an alkali metal and ends with an inert gas. The exception is the first period which starts with hydrogen (a gaseous nonmetal). All this is very significant but still not the most important feature.

Moseley's law yields a simple method for calculating the number of elements in each period of the system:

Period number	1	2	3	4	5	6	7
Number of elements	2	8	8	18	18	32	32

Let us study closely these numbers. The same numbers we have seen in the table giving the numbers of electrons in the electron shells of atoms. Then a simple conclusion can be made, namely, that a certain electron shell of the atoms is filled with electrons to the full capacity as we go over from the first to the last element within a given period. In other words, the number of elements in the period is equal to the number of electrons in this shell.

If it were so it would be easy to relate the structure of the periodic system to the structure of the atom.

But in fact this is so only for the first and second periods of the periodic system. They contain two and eight elements, respectively. These are the numbers of electrons in the first and second electron shells. The third electron shell can contain 18 electrons but the third period has eight elements, as the second period.

Well, that is that. The tempting suggestion that the number of elements in a period equals the maximum number of electrons in the electron shell just does not work.

Hence, the periodic system has a more complex structure than a system of successive electron shells.

Now we can answer the above question—the most important thing about the structure of the periodic system is the fact that each two successive periods have the same numbers of elements in them with the

exception of the first period which consists just of hydrogen and helium.

What are the reasons for that?

Steps, rather than a smooth line. This stepwise variation can be explained as follows. In the atoms of hydrogen and helium the *K* shell is filled which can contain the maximum of two electrons. In the helium atom the *K* shell is completed and this is why helium is an inert gas (atoms with completed outermost shells are chemically inactive). According to Bohr's theory, chemical properties of elements depended on the number and distribution of electrons in the outermost shells.

The eight elements of the second period from lithium to neon can have up to eight electrons in the *L* shell which is the outermost shell in their atoms. Neon atoms have eight electrons in the *L* shell, it is completed, and neon, as helium, is an inert gas.

The third period also contains eight elements from sodium to argon. But their outermost electron shell, the *M* shell, can contain up to 18 electrons. Eight electrons appear in this shell by the end of the third period, that is, in argon which is also an inert gas. But then the *M* shell has ten electron vacancies left. In atoms of which elements will they be filled?

The first two elements in the fourth period are potassium and calcium, the typical alkali and alkaline-earth metals. According to what we know about the respective elements in the second and third periods—lithium and beryllium and sodium and magnesium—we must conclude that the filling of the *N* electron shell starts with potassium which opens the fourth period of the periodic system.

The fourth period contains 18 elements. Accordingly,

ten electron vacancies are filled in the M shell and eight electrons are added to the N shell.

Thus, Bohr made the important conclusion that starting from the M shell the electron shells in atoms are not filled continuously until they are completed (as it happens with the K and L shells). At some point the filling of one shell is stopped and electrons appear in the other electron shells so that the filling has a stepwise character.

A natural question to ask here is how it all related to the mystery of the rare-earth elements. How long have we to wait for its solution? But have not we repeatedly said that the road to truth is a long and hard one? The impatient reader has to wait.

It was only the complete theory of the periodic system that provided the key to the rare-earth mystery. In this theory the atomic structure is described in terms of the electron “language”.

A wonderful language of four letters. This peculiar language makes use of only four letters. These letters are n , l , m_l and m_s ; they are known as quantum numbers in atomic physics.

“Words” made up of these four letters in various combinations can “describe” the state of any electron in the atom of any chemical element. But there is nothing magical about these letters, what they reflect is the physical reality.

We are already acquainted with the quantum number n as we have met it in the expression $2n^2$ for the number of electrons in an electron shell. Thus, n is the number of the electron shell, that is, it shows to which shell the electron belongs.

The quantum number n is known as the principal quantum number, its values are integers 1, 2, 3, 4, 5,

6, 7, ... corresponding to the electron shells K, L, M, N, O, P, Q .

The quantum number n appears in the formula for the electron energy and so we can say that it describes the electron energy in the atom.

The orbital (or azimuthal) quantum number determines the shapes of different electron orbits belonging to the electron shell with a given n .

Each electron shell (with the exception of the first one) consists of a number of subshells, their number is equal to the number of the shell. Thus, the K shell ($n = 1$) has one subshell, the L shell ($n = 2$) has two subshells, the M shell ($n = 3$) has three subshells and so on.

Each subshell of a given electron shell is described by the appropriate value of the orbital quantum number. These values are also integers but starting with the zero, that is, 0, 1, 2, 3, Thus, l cannot be more than or equal to n . For $n = 1$ we have $l = 0$, for $n = 2$ we have $l = 0$ and 1, for $n = 3$ we have $l = 0, 1$ and 2 and so on. In general, l varies from 0 to $n - 1$.

In atomic physics the electron subshells are traditionally designated with the letters s ($l = 0$), p ($l = 1$), d ($l = 2$), f ($l = 3$) and so on.

The following table presents the designation of the electron subshells in the atom:

Shell	Subshell			
K ($n = 1$)	$1s$ ($l = 0$)			
L ($n = 2$)	$2s$ ($l = 0$)	$2p$ ($l = 1$)		
M ($n = 3$)	$3s$ ($l = 0$)	$3p$ ($l = 1$)	$3d$ ($l = 2$)	
N ($n = 4$)	$4s$ ($l = 0$)	$4p$ ($l = 1$)	$4d$ ($l = 2$)	$4f$ ($l = 3$)

and so on.

The numbers before the letters s , p , d , f are the principal quantum numbers. For instance, the electrons in the $4s$ subshell are described by the principal quantum number $n = 4$ and the orbital quantum number $l = 0$.

The two quantum numbers n and l are all that we need to explain the structure of the periodic system in the electron “language” if we know how many electrons can be accommodated in various electron subshells.

These electron numbers are determined by the third and fourth quantum numbers, i.e. the magnetic quantum number m_l and the spin quantum number m_s .

The quantum number l describes the shape of the electron orbits. The magnetic quantum number m_l is related to l ; it determines the orientation of these orbits in space and their number for a given l value. For a given l the quantum number m_l has $(2l + 1)$ values from $-l$ to $+l$ including zero. For instance, for $l = 2$ we have five values of m_l : -2 , -1 , 0 , $+1$, $+2$.

The state of each electron in a given electron orbit (with given n and l) is determined also by the spin quantum number m_s , which can have only two values, namely, $+1/2$ and $-1/2$. According to physical laws, each electron orbit cannot accommodate more than two electrons.

Thus, each electron subshell can accommodate the maximum of $2(2l + 1)$ electrons:

$$\begin{array}{ll} s \text{ subshell } 2(2 \times 0 + 1) = 2 \text{ electrons} \\ p \text{ subshell } 2(2 \times 1 + 1) = 6 \text{ electrons} \\ d \text{ subshell } 2(2 \times 2 + 1) = 10 \text{ electrons} \\ f \text{ subshell } 2(2 \times 3 + 1) = 14 \text{ electrons} \end{array}$$

As mentioned above, no two electrons in the atom can have the same set of four quantum numbers n ,

l , m_l and m_s . This is a consequence of the physical law known as the Pauli exclusion principle (after the Swiss theoretical physicist Wolfgang Pauli). If we know the number of electrons in a given atom which is equal to its number in the periodic system we can “construct” the atom and calculate the structure of its outermost electron shell.

Now we have everything needed to describe the periodic system in the “electron” language and to explain the periodic variation of the chemical properties of elements.

Periodic variation of the electron shells. Mendeleev established that if the elements were arranged in the order of increasing atomic weight the chemical properties of elements were periodically repeated in such element series.

Bohr found a similar regularity for the electron shells—similar types of the outermost electron shells are periodically repeated in the series of elements with increasing atomic numbers. For instance, all alkali metals have one s electron in the outermost electron shell and all inert gases (with the exception of helium) have six p electrons there.

Thus, the chemical similarity between elements is due to the similarity in the structure of the outermost electron shells of their atoms. The periodic variation of the chemical properties of elements is caused by the periodic repetition of the similar electronic configurations of the atoms.

Thus, the properties of chemical elements are directly related to the structure of their atoms or, more exactly, to the numbers and arrangement of electrons in the outermost electron shell (and frequently the one immediately before it).

These are the fundamental concepts of the theory explaining the periodic system of elements.

When the periodic system had been written down in the “electron” language it immediately acquired a new, physical meaning.

Let us describe the elements in this language.

Since the first and second periods of the periodic system correspond to the completed *K* and *L* electron shells the “electronic structure” of these periods can be written as follows:

First period (H—He): $1s^2$.

Second period (Li—Ne): $2s^22p^6$.

Since the third period (Na—Ar) is similar to the second period its “electronic” formula is $3s^23p^6$.

But where are ten electrons from the $3d$ subshell? They will appear in the atoms of subsequent elements but not immediately. In the fourth period filling of the $4s$ subshell starts in potassium and calcium and filling of the $3d$ subshell starts only in scandium which follows calcium. Filling of the $3d$ subshell is completed in zinc. The $4p$ subshell is filled starting with gallium and ending with krypton.

Now we can easily write down the electron structure of the fourth period (K—Kr): $4s^23d^{10}4p^6$. It explains why this period contains 18 elements.

The electron structure of the fifth period (Rb—Xe) is similar to that of the fourth period and we can easily write for it $5s^24d^{10}5p^6$.

Now we have reached the sixth period, the one that contains the rare-earth elements. The “electron” language gave an amazingly simple explanation of the surprising similarity of their properties that baffled scientists for many years. But before telling about it we have to make a short introduction.

The great achievement of Bohr was not only that he correctly described how the electron shells and

subshells in atoms were filled. He also skillfully used this knowledge to explain the chemical properties of elements.

For instance, why do all alkali metals have such high reactivities? Because their atoms have a single *s* electron in the outermost electron shell. This electron can be easily detached. Then an atom of an alkali metal becomes an ion whose electron structure is identical to that of the atom of the preceding inert gas which is very stable.

Why do the properties of the neighbouring elements in the second and third periods show such a significant difference? For instance, boron greatly differs from beryllium and nitrogen is quite unlike carbon. The explanation is that the addition of an electron to the outermost electron shell expands the valence range of the atom.

But in the larger periods there are ten elements in which the *d* subshell is filled (we shall call them *d* elements). All these elements are metals and the difference between their properties is much weaker than that for the elements in which the *s* or *p* subshells are filled. Why is it so? The explanation is that almost all the *d* elements have identical structures of the outermost electron shell, most of them have two *s* electrons in it. Therefore, the difference between the *d* elements in their "behaviour", so to say, is determined by the difference in the number of electrons in their *d* subshells. But it is not the outermost shell, it is closer to the nucleus, is more strongly coupled to it and has less influence on the chemical properties of the element.

It was Bohr's theory that revealed these features of the electron structure of elements and thus helped to solve the mystery of the rare-earth elements. To understand this explanation better let us analyze the

Mendeleev's Periodic

PERIODS	GROUP OF														
	A I B			A II B			A III B			A IV B			A V B		
1	H			•											
2	3Li 6.94 ₁ Lithium 2s ¹			4Be 9.01218 Beryllium 2s ²			5B 10.81 Boron 2s ² 2p ¹			6C 12.011 Carbon 2s ² 2p ²			7N 14.0067 Nitrogen 2s ² 2p ³		
3	11Na 22.98977 Sodium 3s ¹			12Mg 24.305 Magnesium 3s ²			13Al 26.98154 Aluminium 3s ² 3p ¹			14Si 28.08 ₆ Silicon 3s ² 3p ²			15P 30.97376 Phosphorus 3s ² 3p ³		
4	19K 39.09 ₈ Potassium 4s ¹			20Ca 40.08 Calcium 4s ²			21Sc 44.9559 Scandium 3d ¹ 4s ²			22Ti 47.90 Titanium 3d ² 4s ²			23V 50.941 ₄ Vanadium 3d ³ 4s ²		
	29Cu 63.54 ₆ Copper 3d ¹⁰ 4s ¹			30Zn 65.38 Zinc 3d ¹⁰ 4s ²			31Ga 69.72 Gallium 4s ² 4p ¹			32Ge 72.5 ₉ Germanium 4s ² 4p ²			33As 74.9216 Arsenic 4s ² 4p ³		
5	37Rb 85.467 ₈ Rubidium 5s ¹			38Sr 87.62 Strontium 5s ²			39Y 88.9059 Yttrium 4d ¹ 5s ²			40Zr 91.22 Zirconium 4d ² 5s ²			41Nb 92.9064 Niobium 4d ⁴ 5s ¹		
	47Ag 107.868 Silver 4d ¹⁰ 5s ¹			48Cd 112.40 Cadmium 4d ¹⁰ 5s ²			49In 114.82 Indium 5s ² 5p ¹			50Sn 118.6 ₉ Tin 5s ² 5p ²			51Sb 121.7 ₅ Antimony 5s ² 5p ³		
6	55Cs 132.9054 Cesium 6s ¹			56Ba 137.3 ₄ Barium 6s ²			57La* 138.905 ₅ Lanthanum 5d ¹ 6s ²			72Hf 178.4 ₉ Hafnium 5d ² 6s ²			73Ta 180.947 ₉ Tantalum 5d ³ 6s ²		
	79Au 196.9665 Gold 5d ¹⁰ 6s ¹			80Hg 200.5 ₉ Mercury 5d ¹⁰ 6s ²			81Tl 204.37 Thallium 6s ² 6p ¹			82Pb 207.2 Lead 6s ² 6p ²			83Bi 208.9804 Bismuth 6s ² 6p ³		
7	87Fr [223] Francium 7s ¹			88Ra 226.0254 Radium 7s ²			89Ac** [227] Actinium 6d ¹ 7s ²			104Ku [261] Kurchatovium 6d ² 7s ²			105Ns [260] Nilsborium 6d ³ 7s ²		

* LANTHANIDES

58Ce 140.12 Cerium $4f^1 5d^1 6s^2$	59Pr 140.9077 Praseodymium $4f^3 6s^2$	60Nd 144.24 Neodymium $4f^4 6s^2$	61Pm [145] Promethium $4f^5 6s^2$	62Sm 150.4 Samarium $4f^6 6s^2$	63Eu 151.96 Europium $4f^7 6s^2$	64Gd 157.25 Gadolinium $4f^7 5d^1 6s^2$
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** ACTINIDES

90Th 232.0381 Thorium $6d^2 7s^2$	91Pa 231.0359 Protactinium $6d^1 5f^2 7s^2$	92U 238.029 Uranium $5f^3 6d^1 7s^2$	93Np 237.0482 Neptunium $5f^4 6d^1 7s^2$	94Pu [244] Plutonium $5f^6 7s^2$	95Am [243] Americium $5f^7 7s^2$	96Cm [247] Curium $5f^7 6d^1 7s^2$
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Table of the Elements

ELEMENTS									
A	VI	B	A	VII	B	A	VIII		B
			1H 1.0079 Hydrogen $1s^1$			2He 4.00260 Helium $1s^2$			
8O [8 009] Oxygen $2s^2 2p^4$			9F 18.99840 Fluorine $2s^2 2p^5$			10Ne 20.179 Neon $2s^2 2p^6$			
16S [16 06] Sulphur $3s^2 3p^4$			17Cl 35.453 Chlorine $3s^2 3p^5$			18Ar 39.948 Argon $3s^2 3p^6$			
	24Cr 51.996 Chromium $3d^5 4s^1$		25Mn 54.9380 Manganese $3d^5 4s^2$			26Fe 55.847 Iron $3d^6 4s^2$	27Co 58.9332 Cobalt $3d^7 4s^2$	28Ni 58.70 Nickel $3d^8 4s^2$	
34Se [34 96] Selenium $4s^2 4p^4$			35Br 79.904 Bromine $4s^2 4p^5$			36Kr 83.80 Krypton $4s^2 4p^6$			
	42Mo 95.94 Molybdenum $4d^5 5s^1$		43Tc 98.9062 Technetium $4d^5 5s^2$			44Ru 101.07 Ruthenium $4d^7 5s^1$	45Rh 102.9055 Rhodium $4d^8 5s^1$	46Pd 106.4 Palladium $4d^{10} 5s^0$	
52Te [52 80] Tellurium $5s^2 5p^4$			53I 126.9045 Iodine $5s^2 5p^5$			54Xe 131.30 Xenon $5s^2 5p^6$			
	74W 183.85 Tungsten $5d^4 6s^2$		75Re 186.207 Rhenium $5d^5 6s^2$			76Os 190.2 Osmium $5d^6 6s^2$	77Ir 192.22 Iridium $5d^7 6s^2$	78Pt 195.09 Platinum $5d^9 6s^1$	
84Po [209] Polonium $6s^2 6p^4$			85At [210] Astatine $6s^2 6p^5$			86Rn [222] Radon $6s^2 6p^6$			
106			107			Atomic number Atomic mass ----- 92 U 238.029 Uranium	$7s^2$ $6d^1$ $5f^3$	Distribution of electrons by unfilled and following completed sublevels	

65Tb [65 9254] Terbium $4f^9 6s^2$	66Dy 162.50 Dysprosium $4f^{10} 6s^2$	67Ho 164.9304 Holmium $4f^{11} 6s^2$	68Er 167.26 Erbium $4f^{12} 6s^2$	69Tm 168.9342 Thulium $4f^{13} 6s^2$	70Yb 173.04 Ytterbium $4f^{14} 6s^2$	71Lu $6s^2174.97Lutetium 5d^1 4f^{14}$
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97Bk $7s^2$ [247] Berkelium $6d^1 5f^8$	98Cf [251] Californium $5f^{10} 7s^2$	99Es [254] Einsteinium $5f^{11} 7s^2$	100Fm [257] Fermium $5f^{12} 7s^2$	101Md [258] Mendelevium $5f^{13} 7s^2$	102(Nobelium) [255] (Nobelium) $5f^{14} 7s^2$	103(Lr) [256] (Lawrencium) $5f^{14} 6d^1 7s^2$
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structure of the sixth period which is the one that contains the rare-earth elements.

The sixth period starts as the preceding periods—the *s* electrons that appear in the cesium and barium atoms belong to the sixth (*p*) electron shell. The next element is lanthanum which opens the rare-earth series. When Bohr compared its properties with the properties of the preceding elements in the same group—scandium and yttrium—he assumed that the next electron to appear was a *5d* electron.

Bohr thought that next the filling of the “long-neglected” *4f* subshell had to start. It belongs to the fourth (*N*) shell but remains unfilled even in the atoms of the elements where the *5s* and *5p* electrons have appeared and the *6s* subshell has been filled (in cesium and barium). But now was its turn. It is filled up in the series of 14 elements starting with cerium.

In Bohr’s opinion the *4f* subshell was completed in the lutetium atom, that is, the element No. 71 was the last of the rare-earth elements. Thus, the element No. 72 could not belong to the rare-earth series and the old controversy was resolved in favour of hafnium.

But the *4f* subshell is deep inside the atom and its electrons practically cannot take part in chemical binding. It is much more inert than the *d* subshells. Therefore, the chemical properties of the rare-earth elements are wholly determined by the three outermost electrons—two *6s* electrons and one *5d* electron (that appeared first in lanthanum). This is why all rare-earth elements are so amazingly similar in their chemical behaviour to be typically trivalent. That is how Bohr’s arguments ran.

Such was a simple solution that chemists had long and fruitlessly sought and a physicist finally found.

In 1925 the Norwegian mineralogist Victor Gold-

schmidt suggested the name of lanthanides (or lanthanoids) for the $4f$ elements.

A "periodic system" of the rare-earth elements.

Still some facts in the chemistry of the rare-earth elements could not be satisfactorily explained by the theory of atomic structure.

Lanthanum and lanthanides were known to be as a rule trivalent. But, as with any rule, there were exceptions.

The early studies of Berzelius demonstrated that cerium had two types of oxides (see p. 12). Later cerium was found to be tetravalent in the higher oxide. After von Welsbach had found the components of didymium Brauner managed to prepare the oxide of tetravalent praseodymium. Three more exceptions were found early in the 20th century; they were tetravalent terbium and divalent europium and samarium.

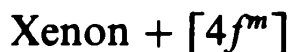
Of course, these exceptions did not substantially change the overall pattern. But there was something unaccountable about them and it made the chemistry of the rare-earth elements not such a boringly obvious subject after all.

The prominent German inorganic chemist Wilhelm Klemm started to work seriously on the rare-earth elements in 1928. First he analyzed the structure of the triply charged ions of lanthanum and lanthanides.

Take, for instance, lanthanum. According to Bohr's theory, its outermost electron shells have the structure $6s^25d$. When the valence electrons are detached the lanthanum atom is transformed into the triply charged ion La^{3+} . One can immediately guess that this ion has exactly the same structure as the atom of the closest inert gas, that is, xenon.

Klemm suggested the following formula for the

structure of all triply charged ions of lanthanides:



It means that the ions of lanthanides contain from 1 to 14 $4f$ electrons in addition to all electron shells and subshells that exist in the xenon atom.

Klemm concentrated his attention on the ion Gd^{3+} which had a half-filled $4f$ subshell ($m = 7$) and the ion Lu^{3+} in which the $4f$ subshell was completed.

Thus, the ions La^{3+} , Gd^{3+} and Lu^{3+} had a similar structure but the last two ions had also $4f$ electrons (7 and 14, respectively). These ions were also similar in many of their properties.

Then Klemm made a surprising suggestion to regard the ions La^{3+} , Gd^{3+} and Lu^{3+} as something like “inert gases” in the series of the rare-earth elements.

Proceeding from this assumption Klemm put forward the following classification of the triply charged ions of the rare-earth elements:

						La^{3+}
Ce^{3+}	Pr^{3+}	Nd^{3+}	Gd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
$4f^1$	$4f^2$	$4f^3$	$(4f^4)$	$4f^5$	$4f^6$	$4f^7$
Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
$4f^8$	$4f^9$	$4f^{10}$	$4f^{11}$	$4f^{12}$	$4f^{13}$	$4f^{14}$

Klemm named this classification “the periodic system of the ions of rare-earth elements” and it was this classification that helped chemists to understand why rare-earth elements had sometimes valences other than 3.

Indeed, if the ions Ce^{3+} and Tb^{3+} lose one electron each they will have the stable (preferable, as Klemm called them) structures of the ions La^{3+} and Gd^{3+} , respectively. Thus, the $4f$ subshell proves to be not so immutable, after all. The praseodymium ion apparently tends to the structure of La^{3+} , too. But it cannot get

rid of both its 4f electrons; it is quite an effort to detach one of them. This is how the oxide PrO_2 is produced. As for the “intermediate” lanthanides they just cannot get rid of any of their 4f electrons.

The europium ion reaches the Gd^{3+} configuration when two-valence electrons are detached, rather than three, which is typically the case for the rare-earth elements. Then we obtain the doubly charged ion Eu^{2+} , that is, divalent europium. Here once more the explanation is quite simple.

The divalent samarium appears also as a result of the samarium ion tending to reach the Gd^{3+} configuration. However, this configuration corresponds to singly charged ion Sm^+ which does not exist and samarium “stops halfway” giving rise to Sm^{2+} .

Klemm used his “periodic system of ions” to predict the existence of divalent ytterbium. The reader can easily understand how he did it. The ion Yb^{2+} was duly found to exist and Klemm’s classification received the best possible support by showing its predictive powers.

Thus a rigorous physical substantiation was obtained for the classification of the rare-earth elements into the cerium group and the yttrium group.

Why are zirconium and hafnium so much alike? Indeed, one can hardly find two other metals (with the exception of the rare-earth metals, of course) whose chemical properties are so similar. It is extremely difficult to separate zirconium and hafnium. This is why the element No. 72 could not be discovered for such a long time—it was masked by zirconium whose natural abundance is much greater.

It is lanthanides that are “responsible” for this close similarity, or, more exactly, the peculiar decrease in

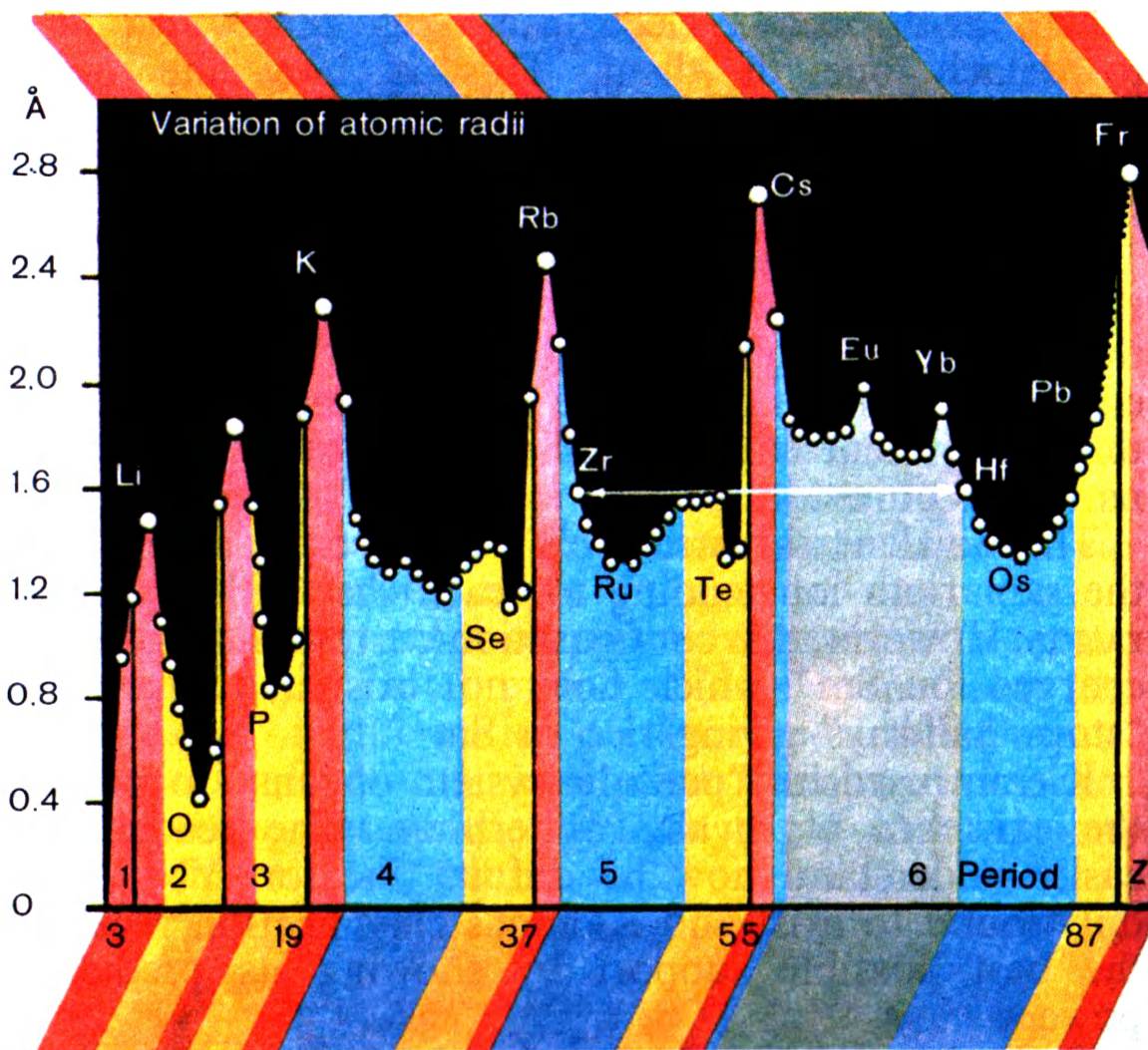


Fig. 10

the atomic radius of the elements from lanthanum to lutetium.

The chemical similarity of lanthanides is explained by the fact that their atoms have close radius.

Figure 10 shows the variation of the atomic radii with the atomic number. We can answer the question heading this section by analyzing this variation.

One can see that the alkali metals which start the periods have the largest atomic radii. This is understandable since a new electron shell starts to be filled in these atoms. In the following elements the atomic

radius decreases rather sharply as the charge of the atomic nucleus increases and a greater attraction force acts on the outer electrons. When the number of the outer electrons increases they behave as if they are pushing one another apart and thus their response to the increase in the nuclear charge becomes less pronounced. The atomic radius is seen to increase somewhat as a result of that.

Such a pattern of variation is typical for the smaller periods of the periodic system, that is, the second period (Li—Ne) and the third period (Na—Ar).

In the larger periods—the fourth (K—Kr) and the fifth (Rb—Xe)—the variation of the atomic radius with increasing atomic number is more irregular in character. In certain ranges of atomic numbers corresponding to the transition metals, that is, the *d* elements, the variation of the atomic radius is relatively small. How can it be explained? The reason is that the *d* electrons act as a shield which weakens the effect of the nuclear charge on the outer electrons. Such a “leisure” decrease in the atomic radius accounts for the rather gradual variation of the properties of the transition *d* elements.

We see in Fig. 10 a region of even slower variation of the atomic radius for the elements of the sixth period which are in fact lanthanides. What is the cause of it? The explanation is that the 4*f* subshell which is filled in the lanthanide atoms also acts as a shield and even a more effective one than that formed by the *d* elements. This 4*f* shield significantly weakens the effect of the nucleus on the outer electrons and as a result the atomic radius of lanthanides varies rather slowly. The atomic radius decreases just by 0.15 Å (the angstrom unit, $1 \text{ Å} = 10^{-8} \text{ cm}$) in the range of 15 elements from lanthanum to lutetium.

The variation of the atomic radius becomes sharper starting with hafnium. But the “inhibiting effect” of lanthanides is such that the atomic radius of hafnium is almost the same as that of zirconium (1.57 Å in Hf and 1.58 Å in Zr). This is why these two elements exhibit an amazing chemical similarity.

The slower decrease in the atomic radii of lanthanides is known as the lanthanide contraction in chemistry. It has a noticeable influence on the chemical properties of the elements in the lower part of the periodic system by making closer the properties of the elements belonging to the subgroups. Not only zirconium and hafnium exhibit highly similar chemical behaviour. Niobium and tantalum and molybdenum and tungsten are also very similar because the atomic radii are very close in these pairs.

Moreover, the peculiar variation of the atomic radius explains why Sc and Y are so similar to La and lanthanides and occur together with them in nature. The fact is that the atomic radius of yttrium (1.80 Å) is close to that of the elements at the middle of the rare-earth series and the atomic radius of scandium is close to that of lanthanum.

Why are the rare-earth elements trivalent? A feature distinguishing the chemical behaviour of the rare-earth elements is that they have the main valence (or the degree of oxidation) of three. This is the primary chemical reason for placing them (all together) into the third group of the periodic system.

We know already that this rule is not without exceptions. Cerium, praseodymium and terbium can be tetravalent; samarium, europium and ytterbium can be divalent. Chemists have prepared compounds of practically all lanthanides in anomalous valence states.

But still the fundamental rule stays—all the rare-earth elements have a valence of three.

But why is it so?

After our discussion of their atomic structure the answer seems quite clear. Because they typically have three valence electrons.

Let us, however, go deeper into it.

Everything is quite straightforward for scandium, yttrium and lanthanum—two valence electrons (*s* electrons) are in the outermost electron shell and one valence electron (*d* electron) is in the preceding shell. The explanation why these elements are trivalent raises no doubts at all.

When we explained the chemical properties of lanthanides proceeding from their atomic structure we assumed that all of them had such a combination of the valence electrons, that is, two *s* electrons and one *d* electron. We also assumed that sometimes one of the *4f* electrons could be used for chemical binding.

This explanation had seemed quite satisfactory until new significant facts were found.

The facts were revealed by spectral analysis which, as we saw, occasionally brought bad luck to the rare-earth science. Though now it was not the old spectral analysis with its lack of rigorous theory and poor experimental techniques. The spectroscopy of today is a powerful and reliable research instrument.

The optical spectra of the rare-earth elements are highly complicated and it took scientists a long time to interpret them correctly.

In the middle of the forties the American spectroscopist William Meggers demonstrated that the structure of many rare-earth atoms was generally somewhat different from what had been assumed earlier.

His major result was that the atoms of most lanthanides did not contain *5d* electrons in the normal

state. Only cerium, gadolinium and lutetium had these electrons. He presented the following scheme:

						La $6s^25d$
Ce $6s^25d4f$	Pr $6s^24f^3$	Nd $6s^24f^4$	61 $6s^24f^5$	Sm $6s^24f^6$	Eu $6s^24f^7$	Gd $6s^25d4f^7$
Tb $6s^24f^9$	Dy $6s^24f^{10}$	Ho $6s^24f^{11}$	Er $6s^24f^{12}$	Tm $6s^24f^{13}$	Yb $6s^24f^{14}$	Lu $6s^25d4f^{14}$

It can be seen that the presence of a valence d electron in the lanthanide atoms is by no means a general rule but rather an exception.

Now remember how we explained the admirable constancy of the trivalent state of lanthanides by the special strength of the $4f$ subshell whose electrons in principle could not be involved in chemical binding. But now when the handy $5d$ electron is out of it this explanation proves to be baseless. Hence, if the $4f$ electrons cannot be used for valence bonds then all lanthanides with the exception of cerium, gadolinium and lutetium must be divalent and only divalent since they have two $6s$ electrons.

But in more than a hundred and fifty years of chemical studies lanthanides were shown to be predominantly trivalent. Or is it again the "sea of errors" that we are seeing here?

In fact, chemists are yet to find an entirely satisfactory and impeccable explanation of the constancy of the trivalent state of lanthanides.

More or less acceptable hypotheses have been put forward. Apparently, the $4f$ subshell is not so unapproachable after all and under certain conditions it "condescends" to make available one or at the most two electrons. Entering into a chemical reaction the lanthanide atom is excited and a $4f$ electron jumps over to the $5d$ subshell. The rest is clear.

In fact, the chemistry of lanthanides still presents quite a few riddles besides the one discussed above.

We shall tell now about one of them which has been debated for a long time with uncertain results.

Lanthanum or lutetium? The question is which of these two elements is a direct chemical analogue of scandium and yttrium? This question can be reworded as follows. What group of elements must be regarded as the lanthanide series and taken outside the periodic table—the cerium-lutetium group or the lanthanum-ytterbium group?

Typically, lanthanum is regarded as the direct “follower” of yttrium in the third group of the periodic system. What are the reasons for that? The balancing electron in the lanthanum atom is a *d* electron as in the atoms of scandium and yttrium.

The reason seems solid enough... However, a small but pertinent feature must be taken into account here.

That the balancing electrons in the atoms of scandium and yttrium are the *d* electrons is the “unshakable” rule according to which the electronic configurations are formed in the atoms of the elements belonging to the fourth and fifth periods. Electrons of any other types cannot appear here in principle.

But lanthanum belongs to the sixth period where the *f* elements appear for the first time. The first of the *f* elements is cerium. Why does it happen to be cerium and no other element?

Let us look once more on the order of the elements starting the periods.

In the second and third periods *s* elements are followed by *p* elements while in the fourth and fifth periods *s* elements are followed by *d* elements.

This indicates a regular variation of the difference between the principal quantum numbers. In the second

and third periods it is zero and in the fourth and fifth periods it is unity (we have $2s$ and $2p$, $3s$ and $3p$, $4s$ and $3d$, $5s$ and $4d$).

Then in the sixth period this difference must be two ($6s$ and $4f$).

But in fact a $5d$ element—lanthanum—appears and the difference remains unity.

This is no accident in the final analysis. The electron shells of atoms are not always filled according to the same rigid scheme. In fact, the appearance of the $5d$ electron in lanthanum is more favourable energetically than the appearance of the $4f$ electron.

This is why lanthanum is usually regarded as a direct analogue of scandium and yttrium.

However, in scandium and yttrium the filling of the d subshells, once started, continues until the d subshells are completed while the successive filling of the $5d$ subshell is resumed only starting from lutetium. When one looks from this viewpoint then one can regard lutetium as the closest “relative” of scandium and yttrium.

Generally speaking, both of these approaches have proper substantiation and it would be wrong to disclaim either of them. The preference given to lanthanum is to a certain extent a matter of tradition.

It is true that many scientists still support this tradition. Their reasoning is that in the series Sc—Y—La many quantitative properties (for instance, the atomic radii) vary in a more regular way than in the series Sc—Y—Lu . These arguments of course must be taken into consideration.

The fact is that at the beginning of the sixth period we encounter the first manifestations of the phenomenon known as “blurring of periodicity”. It seems as if the distinct boundaries between the successive $4f$ and $5d$ subshells were blurred. The $4f$ subshell is actually

filled up in 13, rather than 14, elements (since a 5d electron appears in the gadolinium atom) while 15 elements from lanthanum to lutetium evidence close chemical similarity. This is what lies at the base of the discussion about the immediate analogue of yttrium – lanthanum or lutetium?

New suggestions on the position of the rare-earth elements in the periodic system. Many learned papers on the rare-earth elements could be given such a heading and, alas, more such papers are bound to appear. But why “alas”? Can one say that the position of lanthanides in the periodic system has been determined once and for all? We shall not answer this question immediately.

In 1938 when all the rare-earth elements (with the exception of the element No. 61) had been long discovered and their properties more or less known the German chemist Walter Noddack made his famous remark: “Whenever somebody suggests his version of the periodic system the lanthanum-lutetium series is presented in it in a different way.” Noddack did not exaggerate the situation much if at all. At any rate, he observed a distinct trend.

Noddack suggested the following explanation. Firstly, all 15 elements are allocated only one slot in the periodic system; secondly, no other series of elements has such peculiar (or so similar) properties as the rare-earth series.

To satisfy the first requirement chemists “modify” the periodic system in some way to find a suitable place for lanthanum and lanthanides.

To take into account the second factor chemists classify the rare-earth elements into groups and make up a “small periodic system” as it was done by Wilhelm Klemm.

representations of the periodic system of elements. These two classic versions of Mendeleev's table are quite well known and we shall not describe them here.

The short table is shown on pp. 52-53 of this book. In this table lanthanum and lanthanides are placed in the slot No. 57 which belongs to the subgroup (B) of the third group. Under the table the lanthanide series is given in full.

This is a concise and elegant method of presentation which by no means impairs our understanding of the matter. It clearly displays their notorious chemical similarity and emphasizes that their main valence is three. The lanthanide series under the table can be broken down into two series, cerium-gadolinium and terbium-lutetium. That would be the "small periodic system" mentioned by Noddack.

No better way of presentation could be found.

In the long version of the periodic table the elements of the main groups (A) and the subgroups (B) are presented separately, rather than in the same group. The rare-earth elements are placed within the table but as an independent row without analogues above them.

In short, the arrangement of elements follows the same concept as in the short version of the table. Neither of the versions has any significant advantages or drawbacks when compared to the other one.

However, they have some common drawbacks. In both versions lanthanides prove to be isolated from the rest of the periodic system, from the relationships with other elements. For instance, no account is taken of the fact that cerium is distinctly tetravalent or that europium and ytterbium are divalent.

It is these drawbacks that stimulated and still stimulate many chemists to look for other ways of arrange-

ment of the rare-earth elements in the periodic system.

One may recall that it was Mendeleev who suggested placing the rare-earth elements into various groups though this attempt failed, of course, as it was bound to. But even after that many scientists tried to follow this way. They unsuccessfully kept on searching for at least some limited similarity between the rare-earth elements and their suggested analogues in groups. Attempts were made to do what Noddack called "modifying" the periodic system. This work produced no useful results but no particular harm too, and it left no noticeable trace in the history of the periodic system.

A suggestion was also made to set aside special subgroups in the table for the rare-earth elements. However, it can be compared to pushing a third bed into a hotel room which barely accommodates two.

New suggestions will surely be made with the excellent purpose of finding "a more satisfactory" arrangement of the rare-earth elements in the periodic system. But it can confidently be predicted that all such attempts will be fruitless.

It is just impossible to find a better placement for the rare-earth elements in the periodic table which would take into account all their properties. So it is useless to waste time here; they must be directed to the many yet unsolved problems in the periodic system which are really important.

There was time when even the fundamental textbooks on chemistry dismissed the rare-earth elements with a curt statement: "The properties of these elements are not known well enough; their abundance in nature is very low."

Such an attitude is now a thing of the past. The rare-earth elements are now known as well as many other elements which have been found much earlier.

From the point of view of physics and chemistry. The scientists who pioneered the studies of the rare-earth elements—Gadolin, Berzelius, and even Mosander—did not live to see a pure rare-earth metal. Production of a rare-earth metal proved to be a very difficult task.

Three small bright cubes of lanthanum, cerium and neodymium were shown at the World Exhibition in Paris in 1900. Their production was regarded as a great achievement.

The history of the rare-earth elements was similar to the history of many other elements in that they had been first discovered as oxides and only after some time were prepared in the metallic state. In the case of the rare-earth elements this time was especially long. The first grams of pure holmium, dysprosium, thulium and lutetium were obtained only after the Second World War.

The reason is that the rare-earth oxides are very strongly bound compounds and it is very difficult to reduce metals from them. The conventional chemical procedures used in the last century were not much help. Some rare-earth metals were produced, though, but only as powders and they were far from pure.

First successful results were obtained by electrolysis of molten chlorides. Metal was deposited on cathodes, it was scrubbed off and remelted. Thus the metal ingots shown at the Paris Exhibition were produced.

But the electrochemical technology does not produce metals of sufficient purity. Therefore, they are produced now with the so-called thermal reduction techniques involving high temperatures. A mixture of rare-earth fluorides with metallic calcium is loaded into special steel vessels. Fluorides must be pure and free of water. The mixture is heated up to 1500°C and calcium acts as a reducing agent. Then calcium is eliminated from

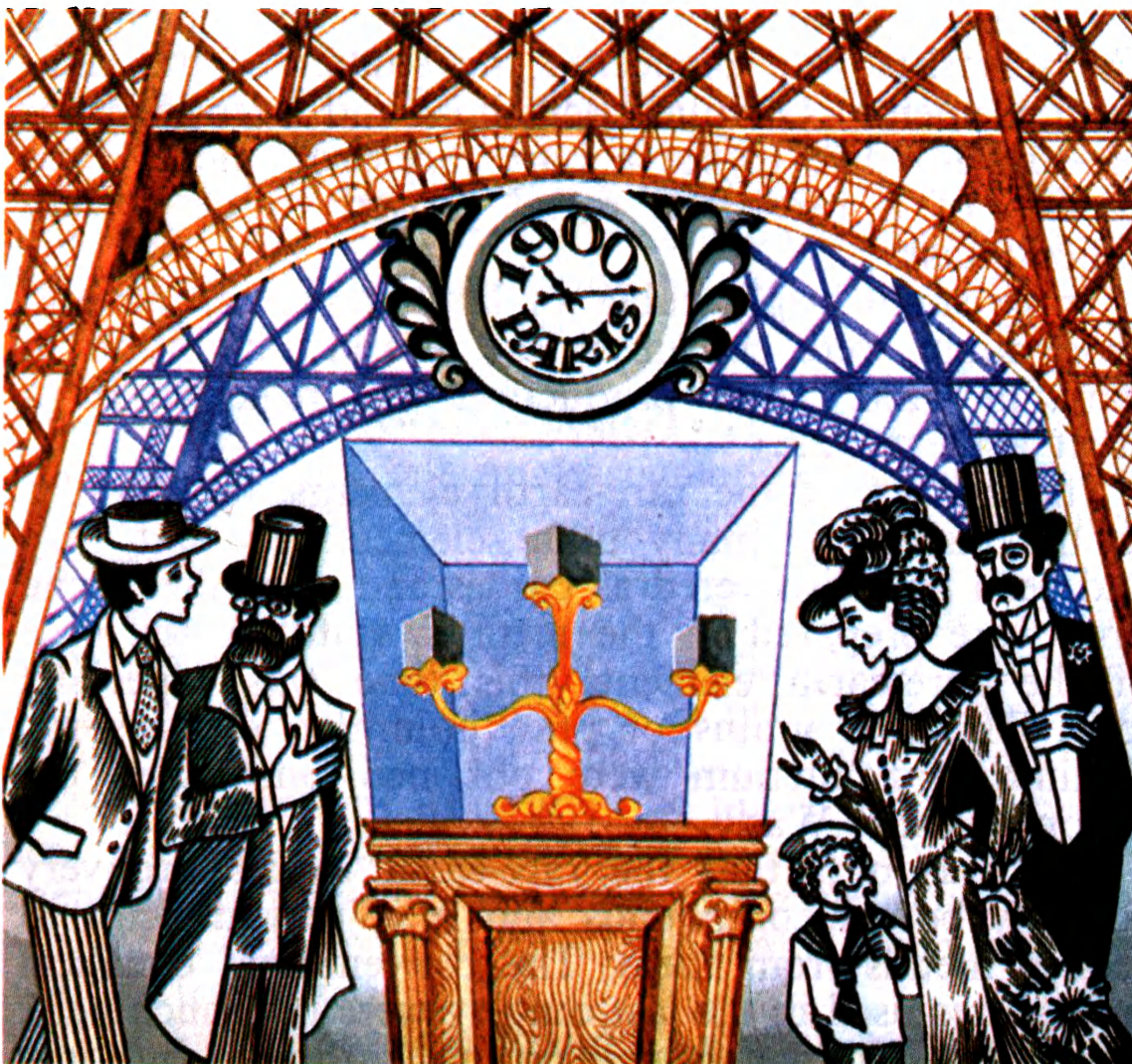


Fig. 12

the product and the rare-earth metals are separated.

Thus, the modern technology makes it possible to produce sufficiently pure rare-earth elements.

Properties of the rare-earth elements. A description of a chemical element is typically started with its appearance. For instance, bromine is a rust-coloured liquid and potassium is a silvery metal. The pure copper is known to have reddish colour. But one can hardly

say something definite about the colour of the rare-earth metals. It depends on many factors, for instance, on the treatment of the surface and the conditions under which the metal was stored. Generally, the rare-earth metals are bright and resemble pure iron or silver with the colour varying from chestnut to dark brown. An oxide film on the metal surface can significantly change its colour.

Physically, the rare-earth metals can be described as being "middle-of-the-road".

They are located at the middle of the periodic system, though a little closer to its end. They have intermediate densities; lanthanum is the lightest (6.16 g/cm^3) and lutetium is the heaviest (9.85 g/cm^3). Their melting temperatures also have intermediate values; cerium has the lowest melting point (798°C) and lutetium the highest (1675°C).

The density and the melting temperature increase steadily as we move across the rare-earth series with the exception of europium and ytterbium whose densities and melting points are noticeably lower than those of the preceding elements.

The explanation is that europium and ytterbium in the metallic state are mainly in the form of doubly charged (rather than triply charged) ions. They have larger atomic volumes and a different crystal structure which is less strong than that of lanthanum and other lanthanides.

But from the chemical point of view the rare-earth metals can hardly be called "middle-of-the-roads". Lanthanum and lanthanides have high chemical reactivities. They readily react with many nonmetals. They ignite and burn brightly when heated to 400°C . They are rapidly oxidized in damp air becoming coated with a thin oxide film.

Cerium has perhaps the highest reactivity among

lanthanides. A cerium powder is capable of self-ignition. Cerium readily reacts with nitrogen and sulphur. Incidentally, cerium sulphide has the highest melting point among all metal sulphides. Titanium could be melted in a crucible made of cerium sulphide.

The rare-earth metals are easily dissolved by such classic acids as nitric, sulphuric and hydrochloric acids.

Their oxides exhibit a fairly wide range of colours. The oxides of lanthanum, gadolinium, ytterbium and lutetium are colourless. The lower oxide of cerium, Ce_2O_3 , is also colourless but its higher oxide, CeO_2 , has a reddish colour. The oxides of praseodymium and neodymium have the greenish and light bluish colour, respectively. One may recall that praseodymium was named for the colour of its salts (from the Greek for "leek green"). The oxides of erbium, thulium and europium have a light rose-pinkish tint while the oxides of samarium, dysprosium and holmium have a yellowish colour.

Hydroxides of the rare-earth elements also have interesting features. They are very strong bases, the strongest among all hydroxides of trivalent metals. They exhibit practically no amphoteric properties (a capability of reacting chemically either as an acid or as a base). The triply charged ions of lanthanides act as cations in numerous compounds. Only the hydroxide of tetravalent cerium exhibits a weak amphoteric property (for instance, salts of the cerium acid are known).

The rare-earth elements form a large variety of complex compounds.

Separation of the rare-earth elements. In the early days of the history of the rare-earth elements stimulated by the discoveries of Mosander it became abundantly clear to scientists that separation of the rare-earth elements was a colossal task. Indeed, it was perhaps

the single most difficult task in inorganic chemistry.

For almost a hundred years chemists had at their disposal only two methods for separating components from mixtures. We have already mentioned them, namely, the fractional crystallization and the fractional precipitation. It goes without saying that they produced results. However, the price was too high. For instance, more than eight months of hard work and over 5000 recrystallization operations were needed to obtain praseodymium of 99% purity. The thulium oxide of the same purity was produced after six years of continuous hard efforts.

In our time chemists just cannot afford such a waste of time. Though classical separation methods are still employed in laboratories and industry an essentially new technique plays now a major role in separation of rare earths. It is the ion exchange chromatography using the so-called ion exchange resins.

The ion exchange resins are high-molecular organic compounds (polymers) that can adsorb various compounds at their surface. The mechanism of adsorption is such that the positively charged ions of the adsorbed compounds replace the positively charged ions (cations) of the resin or the negatively charged ions (anions) are replaced. The first type of resins is known as cation exchange resins, the second as anion exchange resins.

The rare-earth elements are typically separated with the use of the cation exchange resins. The separation process consists of the following stages.

A special chromatographic column is packed with small resin grains. Then a solution of mixed salts of the rare-earth elements is passed through the column. Their cations are exchanged with those of the resin.

The next stage is the preparation of the washing (so-called eluting) solvent. It includes compounds that can form complex compounds with the cations of the

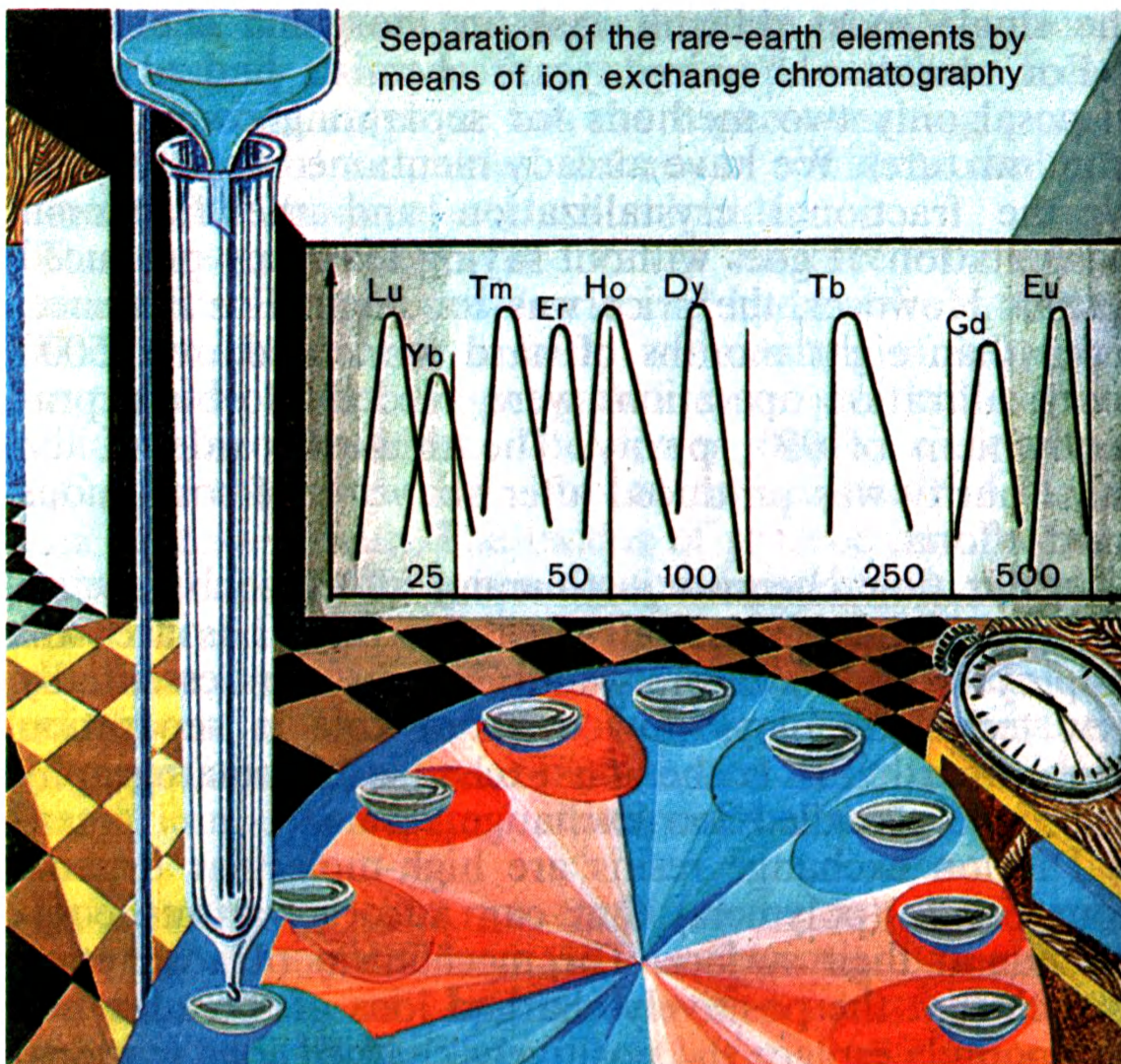


Fig. 13

rare-earth elements. Organic acids, for instance, lactic and citric acids, are typically used as the eluting solvents.

The subsequent course of the process depends on how stable these complex compounds are. The rare-earth cations move downwards in the column under the effect of the eluting solvent. The stabler the complex compound being formed the faster the washing-out of the respective rare-earth cations. Therefore the cations are washed out from the column in a certain order

and can be separated into fractions. The first to be washed out from the column are the fractions containing lutetium and the last are the fractions containing lanthanum.

The ion exchange chromatography produces sufficiently pure lanthanum and lanthanides in a relatively short time.

From the point of view of geology and geochemistry. More than a century of the rare-earth history was based in fact on only three minerals—gadolinite, cerite and samarskite. It was in these minerals that all members of the amazing family of the rare-earth elements were discovered (with the only exception of promethium, of course, which will be discussed below).

Now we know that these three minerals constitute just a tiny fraction of the wide variety of the rare-earth minerals. Even a short description of them would take many pages.

Geologists and geochemists found the rare-earth elements in almost 250 minerals on Earth. In some of them the rare-earth elements are the main components and in many others they appear as impurities.

Soon after the first space flight in history by the Soviet cosmonaut Yuri Gagarin the Soviet geologists found a new rare-earth mineral and named it gagarinite. But gagarinite is by no means the last in the list of the rare-earth minerals and nobody can say when this list is to be completed.

Another interesting fact about the rare-earth elements is that they are always present as trace elements in soil, in animal tissues and in plants. Soils contain up to 0.02% of rare earths and the plant ash contains up to 0.005% of rare earths. The highest concentrations of rare earths were found in lupine and sugar beet. It is still unclear why these widely cultivated crops accu-

multate rare earths. The part played by rare earths in the animal tissues is also unclear. Some scientists believe that they are involved in the growth of the bone tissues.

The rare-earth elements have even been found in the distant stars by astrophysicists. The lunar soil specimens also contain their traces.

In short, it would not be an exaggeration to say that the rare-earth elements are omnipresent.

It was at the very beginning of this book that we questioned the application of the adjective "rare" to these elements. It took scientists many years to show that indeed the rare-earth elements are not rare at all.

There was time when any description of the abundance of elements in the earth crust could be reduced to just one of two words—much or little. Some elements were regarded as common and others as rare. A very simple classification but unfortunately it proved to be wrong. For instance, no geochemist now would say that copper, silver, gold or mercury are common elements. But man had known these elements from time immemorial, widely used them and came to think that there was "much" of them.

As for the rare-earth elements, from the very beginning of their history there was too "little" of them.

To understand the real abundance of elements scientists had to analyze chemically a great variety of ores and minerals.

That was the task of a new science known as quantitative geochemistry. It was pioneered by the American geologist Frank Clarke in the last three decades of the 19th century.

He made heroic efforts indeed having collected and classified the analysis results for more than five and a half thousand specimens of various ores and minerals. It was his work that gave us the first knowledge of what

the earth crust really consists of. The rude classification "much-little" was replaced with exact calculations describing "how much".

The following facts became known as a result of this work. Oxygen is the most common element on Earth. It accounts for half of the mass of the earth crust. The content of silicon is about half as much. Aluminium, iron and sodium are the following common elements. The light elements from hydrogen to iron account for 99.7% of the earth crust. All other elements (more than sixty) account for the remaining small fraction. Thus, the abundance of copper, silver, gold and mercury seems quite negligible.

Now we know that different abundances of elements on Earth are by no means accidental. Scientists have found that the concentration of an element depends on the stability of its atomic nucleus. The abundance of the elements with even atomic numbers (whose nuclei contain even numbers of protons) is much greater (they account for 86% of the mass of the earth crust) than that of the elements with odd numbers. The chemical elements were synthesized many billions of years ago in the vast region of the Universe where our Galaxy is now. Various elements appeared at different stages of evolution of the stars. The nuclear reactions in which elements are produced are governed by laws which are determined, in particular, by different stabilities of the nuclei. This is why different amounts of various elements were produced. The light elements with small nuclear charges were produced in the greatest quantities since such nuclei have the greatest stability.

The chemical composition of Earth, as we know it, springs from this starting uneven distribution of elements.

All this became known long after Clarke's studies. The scientific community honoured the American geo-

chemist by giving the name "clarke" to the unit of the average abundance of an element in the earth crust expressed as a percentage (also known as crustal abundance).

But Clarke could not produce any results on the abundance of the rare-earth elements because in his time only a few rare-earth minerals were known as we have mentioned above. Only later when dozens more rare-earth minerals were found the real abundance of these elements could be estimated.

The decisive contribution to these studies was made by the outstanding Soviet scientists Vladimir Vernadsky and Alexander Fersman.

In the twenties Fersman discovered on the Kola Peninsula gigantic deposits of the mineral apatite which consisted mainly of calcium phosphate. Analyses demonstrated that it contained over 3% of the rare-earth minerals. Similar results were obtained for apatite from other deposits. The reserves of apatite on Earth are very large and from these data Fersman could evaluate the actual content of the rare-earth elements in the earth crust.

Looking at the modern data on the abundance of elements one sees a veritably amazing picture. The rare-earth elements together occupy the 25th place in the list of elements in the order of decreasing abundance. From 10 to 100 grams of cerium and neodymium are found in one tonne of the crustal material. In other words, the amount of these elements on Earth is greater than the amounts of tin, tungsten, cadmium, arsenic, mercury, iodine and uranium. The concentration of ytterbium, dysprosium, gadolinium, samarium, erbium, lanthanum, praseodymium, holmium, thulium and terbium is as high as 10 grams per tonne, that is, higher than the concentration of antimony, bismuth and silver. Even the rarest of the rare-earth elements,

europium, is much more abundant than the platinum metals and gold.

The content of the rare-earth elements on the whole is:

2 times that of tin, 10 times that of lead, 320 times that of antimony, 1600 times that of silver, 2500 times that of mercury, 32000 times that of gold.

Such are the real figures describing the abundance of the rare-earth elements.

The facts presented above are clearly illustrated by Fig. 14 which shows the abundances of all chemical elements. For the sake of convenience the logarithms of the abundances are plotted in the figure so that the points for oxygen and silicon are at almost the same level, though the content of silicon is half that of oxygen. The position of the peaks of the rare-earth elements (they are shown on an enlarged scale) shows that they can hardly be called rare. At the same time one of the primary rules of geochemistry is illustrated here—the abundance of the elements with even numbers is noticeably higher than that of the elements with odd numbers. Yttrium and scandium are not shown on the enlarged scale. The abundance of yttrium is not much lower than the abundance of cerium and it is not surprising that both these elements were the first to be discovered in the rare-earth series. Scandium occupies an intermediate position among the rare-earth elements in this graph.

Given below are the abundances (in weight percent) of the rare-earth elements in the decreasing order:

Ce	Nd	Yb	Gd	Dy	Sm	La
2.9×10^{-3}	1.7×10^{-3}	8×10^{-4}	7.5×10^{-4}	7.5×10^{-4}	7×10^{-4}	6.5×10^{-4}
Er	Pr	Lu	Tb	Ho	Tm	Eu
6.5×10^{-4}	4.5×10^{-4}	1.7×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}	2×10^{-5}

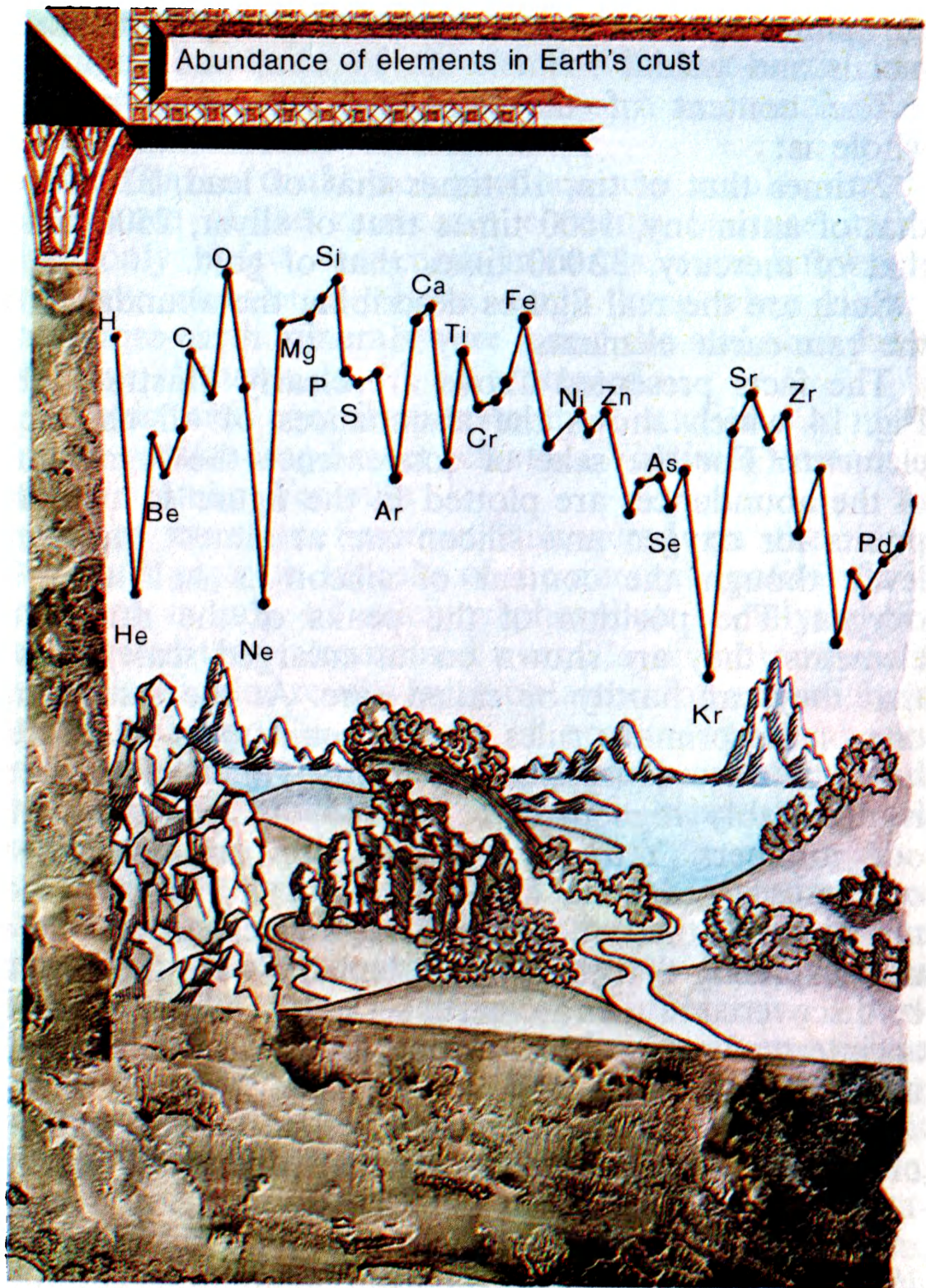
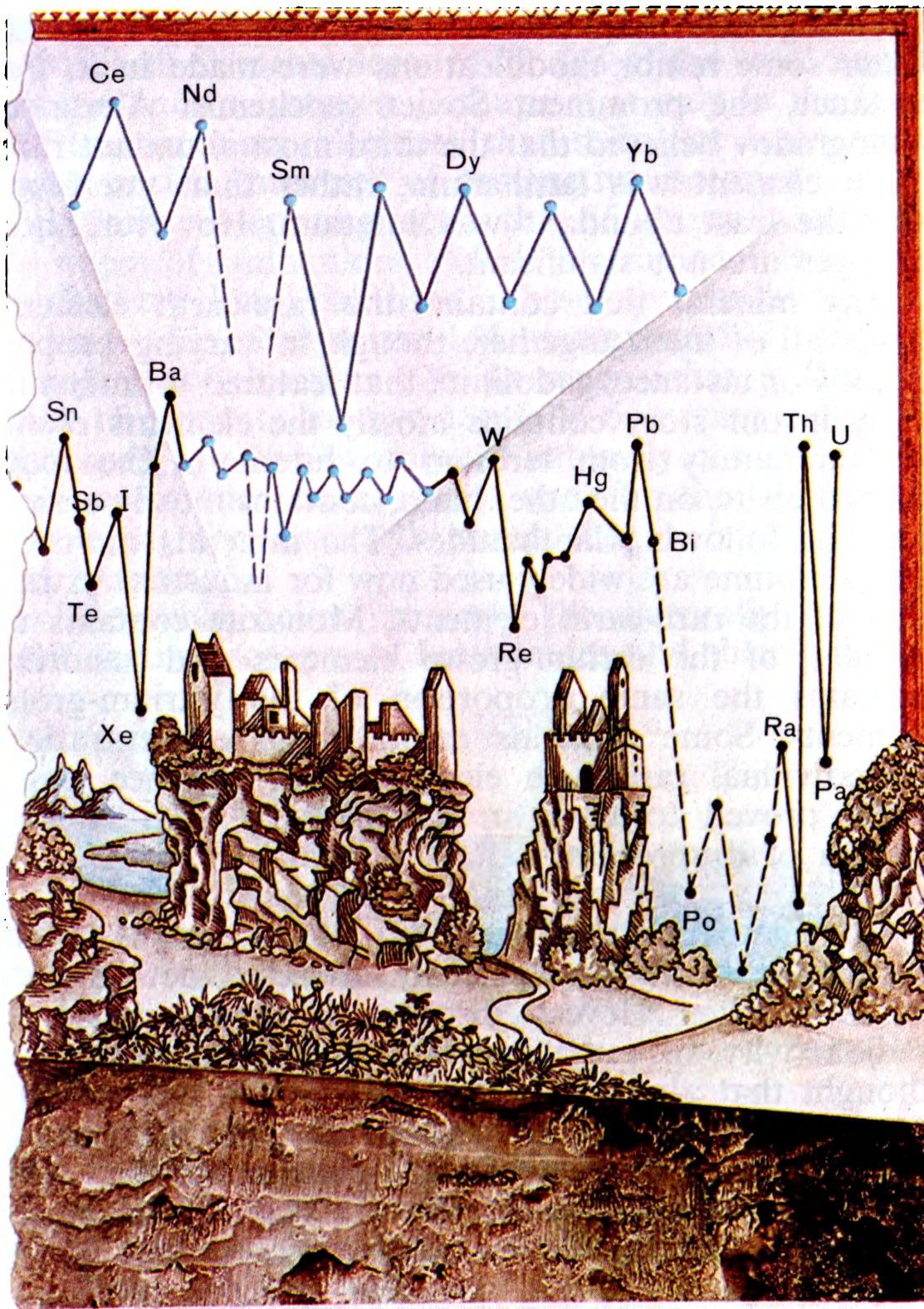


Fig. 14



This general sequence was established by Fersman. Later some minor modifications were made in it. For instance, the prominent Soviet geochemist Alexander Vinogradov believed that the third most abundant rare-earth element was lanthanum, rather than ytterbium, and the least abundant was lutetium. However, these changes are not significant.

Any mineral that contains the rare-earth elements holds all of them together, though in varying proportions. For instance, gadolinite that featured prominently early in our story contains mostly the elements of the yttrium family from terbium to lutetium. The long-known cerite, on the other hand, contains mostly cerium and the following lanthanides. The minerals monazite and xenotime are widely used now for industrial extraction of the rare-earth elements. Monazite contains up to 60% of the cerium-group elements and xenotime contains the same proportion of the yttrium-group elements. Some minerals exhibit high concentrations of individual rare-earth elements. For instance, gagarinite proved to have an unexpectedly high concentration of dysprosium.

From the point of view of nuclear physics. The lanthanide family unexpectedly attracted new interest in 1932 when Hevesy discovered natural alpha-ray radioactivity of samarium. Until then scientists had thought that alpha-ray decay was typical only for the heavier elements at the end of the periodic system starting from polonium. It was perhaps the first indication that this family of elements would prove to be no less fascinating for nuclear physicists than it was for chemists.

Later discoveries amply demonstrated it.

Fifty-five stable isotopes of the rare-earth elements have been found in nature and more than 150 radio-

active isotopes have been produced artificially. The rare-earth elements account for 1/8 of the total number of the known isotopes. Perhaps, it is only in the family of transuranium elements that scientists have reaped such a rich "harvest" of radioactive isotopes.

Another interesting fact is that 55 naturally occurring isotopes of lanthanides include six radioactive isotopes with very long half-lives. These are lanthanum-138, cerium-142, neodymium-144, samarium-147, gadolinium-152 and lutetium-176. It means that a family of just 15 elements has five naturally occurring radioactive isotopes. Meanwhile, only ten naturally occurring radioactive isotopes have been found for the 56 elements preceding the rare-earth group, that is, from hydrogen to barium.

The table below presents the naturally occurring radioactive isotopes of lanthanides and their half-lives:

Isotope	Half-life (year)
^{138}La	1×10^{11}
^{142}Ce	5×10^{15}
^{144}Nd	2×10^{15}
^{147}Sm	1.1×10^{11}
^{152}Gd	1×10^{14}
^{176}Lu	5×10^{10}

All these isotopes can be seen to have very long half-lives.

Most of the radioisotopes of lanthanides, both artificial and naturally occurring, have a tendency to beta-ray decay, that is, they emit either electrons or positrons. However, there are also 16 naturally occurring and artificial alpha-ray isotopes including the samarium isotope first discovered by Hevesy.

Theoretical physicists have explained the mechanism of alpha-ray decay in some lanthanide isotopes by

by a special Commission on atomic weights and some of them were corrected from time to time on the strength of new measurements). Unfortunately, Brauner gave only rounded-off atomic weights.

There are various interesting things in this table for a historian of the periodic system. Note, for instance, the peculiar representation of Brauner's interperiodic group of lanthanides.

But what is much more interesting in the context of this book is the marginal note written by Brauner in German: "NB! 61 ist das von mir 1902 vorhergesagte fehlende Element!" (61st is the missing element predicted by me in 1902). The symbol NB means that Brauner considered that note important.

Could not it be a mystification of some kind? One may recall what was told in the first chapter about the confusion that had prevailed in the rare-earth studies for a long time. Could one dare at the time to predict the existence of a new unknown element? And not only predict it but even assign it a definite place between neodymium and samarium.

However, Brauner was a sober-minded scientist and if he chose to claim anything that meant that he was sufficiently confident of it.

Now that we are about to tell the story of the element No. 61 we see that it had started long before the time when scientists obtained the first grains of it. In addition, the history of this element is perhaps more difficult and intricate than that of any other rare-earth element.

Indeed, the rare-earth element that had its place between neodymium and samarium several times put its appearance in the chemical scene and almost each time it proved to be a phantom. It was given at least three different names before the one we use now – promethium.

Zeichener des Prof. v. H. Brauer
Pag. II

Mendeljew's Periodisches System.

Gruppe: I	II	III	IV	V	VI	VII	VIII	
R ₂ O	R ₂ O ₂	R ₂ O ₃	R ₂ O ₄	R ₂ O ₅	R ₂ O ₆	R ₂ O ₇	R ₂ O ₈	R ₂ O ₉ R ₂ O ₆ R ₂ O ₄ R ₂ O ₃
			RH ₄	RH ₃	RH ₂	RH	(R)	Höchste Oxyde höchste flüchtige H ₂ -Verbindungen
R	R	R	R	R	R	R	R und R	Positive } Maximale Negative } Valenz
Reihe:							R	
1. H 1008							4	2. Periode
2. Li 6	Be 9	B 11	C 12	N 14	O 16	F 19	Ne 20	3. Periode
3. Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35	Ar 36	4. Periode
4. K 39	Ca 40	Sc 45	Ti 48	V 51	Cr 52	Mn 54	Fe 55	5. Periode
5. Rb 85	Sr 87	Y 89	Zr 90	Nb 93	Mo 96	Co 99	Ni 101	6. Periode
6. Cs 132	Ba 137	La 139	Ce 140	Pr 140	Nd 142	Pm 144	Sm 150	7. Periode
7. Fr 223	Ra 226	Ac 227	Th 232	Pa 231	U 238	Np 237	Pu 244	8. Periode
8. Li 6	Be 9	B 11	C 12	N 14	O 16	F 19	Ne 20	9. Periode
9. Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35	Ar 36	10. Periode
10. K 39	Ca 40	Sc 45	Ti 48	V 51	Cr 52	Mn 54	Fe 55	11. Periode
11. Rb 85	Sr 87	Y 89	Zr 90	Nb 93	Mo 96	Co 99	Ni 101	12. Periode
12. Cs 132	Ba 137	La 139	Ce 140	Pr 140	Nd 142	Pm 144	Sm 150	

MS 61 not known until 1902 when it was found in the library of the University of Cambridge.

Fig. 15

Promethium has one special feature that distinguishes it from all other lanthanides.

It does not exist on Earth!

This is why the long history of this element was full of confusion and errors. Perhaps, now that we have stated that the element No. 61 cannot be found in nature this story will not be so absorbing, it will resemble a crime story where the criminal is named in the first page. However, this story is highly instructive and we would not want to miss it.

Back to the eighties. Once again the main hero of the story is Bohuslav Brauner. He was Mendeleev's friend and a staunch supporter of the periodic system and he decided to eliminate the difficulties that still remained in the system.

The Czech chemist chose for himself an arduous task—to solve the problem of didymium which many scientists tried to tackle. Brauner aimed at obtaining the pentavalent didymium. If he succeeded the placement of the rare-earth elements in the periodic table would be much easier.

Brauner's work took many years. He processed numerous specimens of the rare-earth minerals. Day by day he repeatedly separated and purified rare-earth oxides.

What he needed was sufficiently pure didymium.

But when could he say that his material was sufficiently pure? Soon Brauner had to reconsider his aims. He managed to separate his didymium specimen into five fractions which had different molecular weights and alkalinity values.

If we determine from these molecular weights of the oxides the atomic weights of the respective rare-earth elements we obtain the following series:

144.32, 145.10, 145.39, 147.10, 149.40

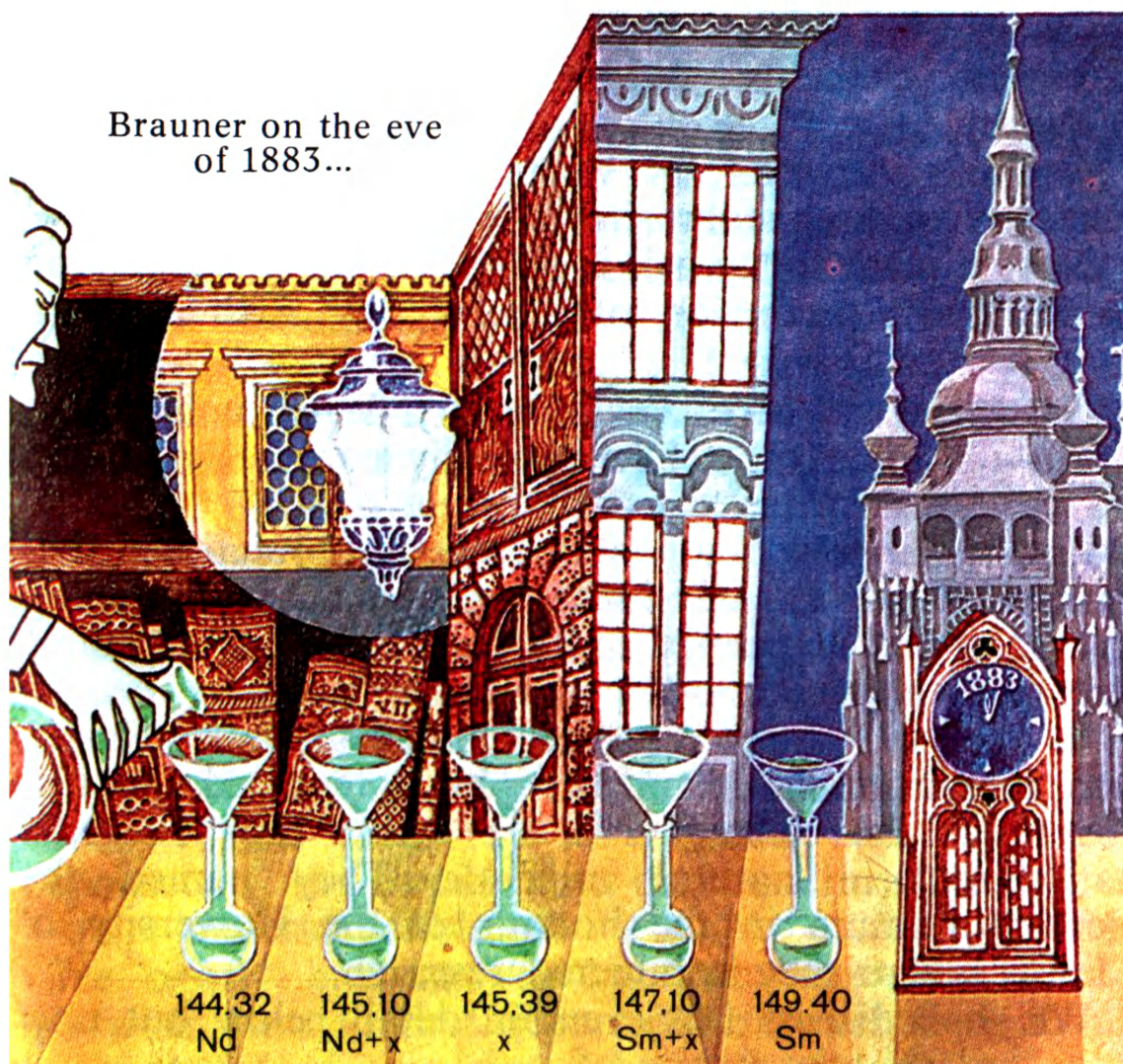


Fig. 16

What conclusions can be drawn from it? Brauner noted in his report that he had managed “to separate didymium into five components—the first, the last and three intermediate ones which are a mixture of the first two”.

He did not mention the pentavalent didymium.

That was what Brauner had achieved by 1883. It is unclear why he discontinued his work on the analysis of the didymium fractions. Soon it became clear that if he had continued his studies he would

have separated the old didymium into two new rare-earth elements. But this honour went to von Welsbach.

Nothing, however, is wasted in science as many centuries of its history show.

Now a reader may ask if all this has any connection to Brauner's prediction of a new rare-earth element.

Unusual analysis of the literature. When a historian works on some subject he typically analyzes it in the chronological order.

But it happens that to understand something that had occurred in the distant past he has to study in detail what happened more recently. This seemingly circuitous approach often proves profitable.

In April 1926 three American chemists – James Harris, Leo Intema and B. Smith Hopkins – reported the discovery of the element No. 61 which they allegedly had found in natural minerals. They named the element illinium in the honour of the University of Illinois where they conducted research.

We shall discuss this event in detail below but now have just to take notice of it.

Incidentally, here is what the American chemists wrote in their report on the discovery of illinium: "There were no theoretical reasons for suggesting that an element existed between neodymium and samarium until Moseley's law demonstrated such a possibility."

In other words, any predictions of the existence of a new element in the rare-earth series were just a waste of time without a physical theory to explain the periodic system.

The report of the American chemists was published in the issue No. 117 of the famous British learned journal *Nature* and a short communication by Brauner was published in the next issue of *Nature*.

Brauner's communication is just half a page long but it tells much. Brauner writes:

(1) that almost all his research work was dedicated to rare earths;

(2) that one of the results of his studies was the separation of the old didymium in 1882;

(3) that another his result was the conclusion that "the gap between neodymium and samarium was too wide" (what he had in mind was the great difference between the atomic weights of Nd and Sm).

Finally, Brauner wrote: "My personal knowledge of the chemical properties of Nd and Sm (I think that the spectral data are too confusing to make conclusions) led me to the assumption that there was an unknown element between them but all attempts to find it with the old methods failed."

Obviously, no scientist can be indifferent about the priority if his discovery is involved and Brauner's response to the report by the American scientists is quite understandable.

He clearly indicated in his communication where and when he had first reported his conclusion about the existence of an element between neodymium and samarium—in an address to a meeting of the Bohemian Academy of Sciences in Prague in July of 1902. It took place half a year after he had delivered a report in Saint Petersburg on his concept of the "inter-periodic group of the rare-earth elements".

Indeed, if one now looks on Brauner's table (see Fig. 6) one can see the empty slot between Nd and Sm.

But Brauner never explained the logic of his reasoning that had led him to his prediction of an unknown rare-earth element. However, his conviction was so strong that one can easily imagine him brooding over the idea of the "eka-neodymium" for many long years.

How could it happen in reality? Let us attempt reconstructing Brauner's reasoning on the basis of what we know about him and his work.

Apart from being an expert on the chemistry of the rare-earth elements, Brauner was a recognized authority on determination of atomic weights.

He measured the atomic weights of neodymium and samarium and of course was concerned about the too great difference between them.

Now one must recall that when Brauner studied didymium in the early eighties he extracted several fractions from it. Later, the first and last fractions were identified as pure neodymium and samarium. But what were the intermediate fractions? They could be mixtures of neodymium and samarium in varying ratios or mixtures of these elements with an unknown element. Brauner apparently supported the second option.

This fact and the too high difference between the atomic weights of Nd and Sm led Brauner to the natural conclusion that there was a gap between these elements.

The story sounds quite mundane but one should not forget the one extraordinary aspect of it, namely, that Brauner predicted an element which did not exist in natural minerals. Of course, Brauner did not and could not know it when he reported this prediction in 1902. Harris, Intema and Hopkins did not know it in 1926 when they reported their discovery of illinium (and nobody knew that at the time).

This was the first time in chemistry that an element which did not exist was predicted and discovered.

The elusive element No. 61. Some ideas have strange histories. Brauner never mentioned his prediction after his report to the Bohemian Academy of Sciences and

up to 1926 (with the exception of the table found among his papers). Moreover, when he suggested in May of 1908 a new placement of the rare-earth elements in the periodic system (in which he dropped for a time his "interperiodic" concept) he did not leave a vacant slot between neodymium and samarium.

But did that mean that Brauner no longer believed in the existence of "eka-neodymium"? It does not seem so. In fact, he said during the discussion of his new hypothesis: "It is highly probable that neodymium will prove to be a complex substance. The jump from Nd-144 to Sm-150 seems to me suspiciously long."

The rigorous physical studies done by Moseley in 1914 indicated that neodymium had the atomic number 60 and samarium 62. From that moment chemists started the race for the discovery of the element No. 61.

A natural question to ask here is why nobody had discovered this element before. After all, the remaining rare-earth elements had been found in various minerals on Earth. Incidentally the elements of the first half of the rare-earth series, that is, belonging to the cerium group, have higher natural abundances than the elements of the yttrium group and hence the element No. 61 should not be all that rare.

Assume now that owing to some unknown laws of nature the element No. 61 is so rare that the accuracy of chemical analysis is just not high enough to find it.

Assume further that owing to some other mysterious laws of nature the properties of the element No. 61 differ sharply from the properties of other rare-earth elements and therefore scientists must look for it not in the rare-earth minerals but in some quite different natural substances.

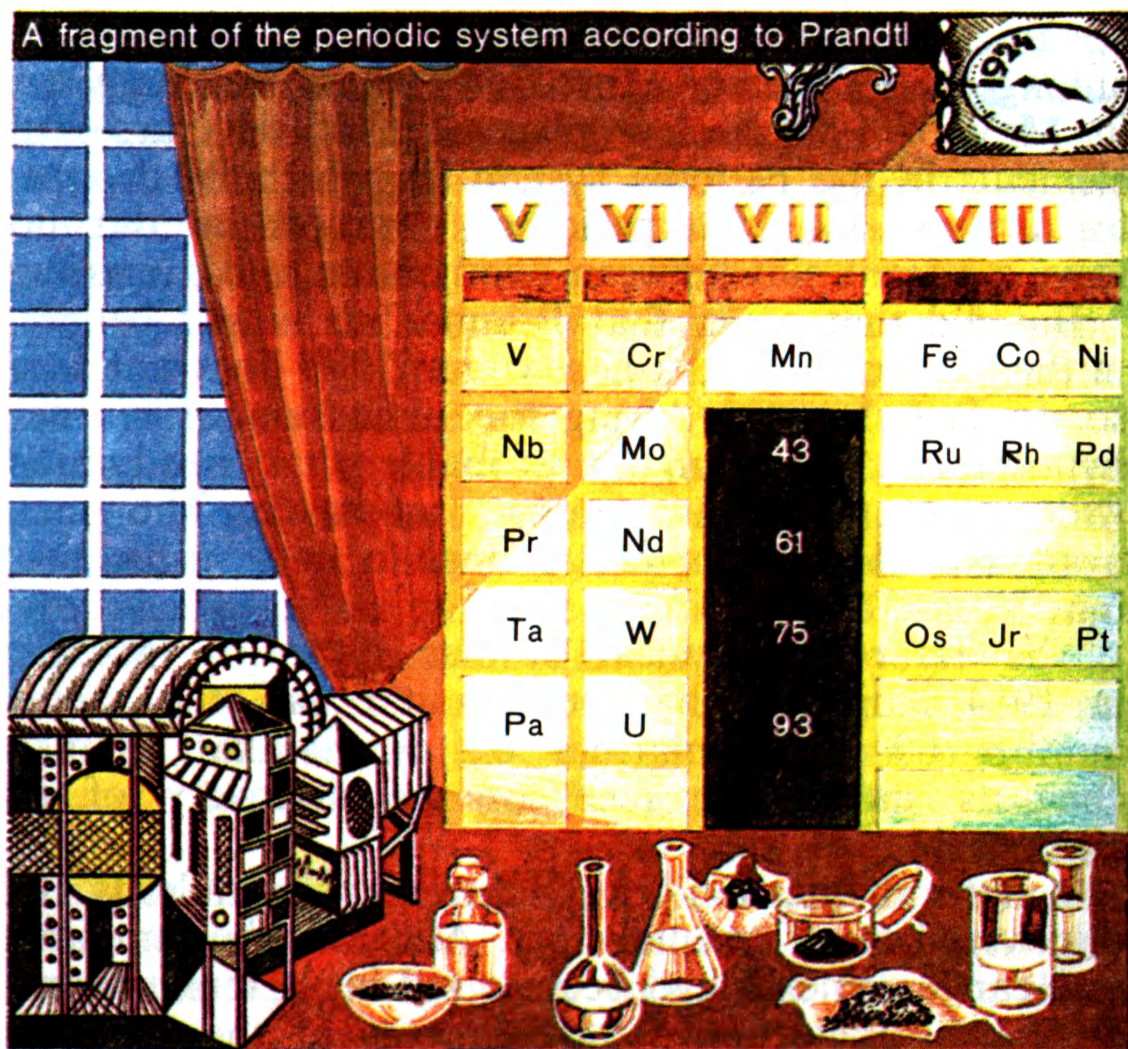


Fig. 17

These two assumptions can serve as a basis for explaining the failure to find this element.

Two German chemists, Wilhelm Prandtl and his young assistant Hans Grimm were perhaps the first to attempt a careful search for “eka-neodymium”. They performed X-ray spectral analysis (that had proved to be of invaluable use in the discovery of hafnium) of more than 50 specimens of rare-earth elements. The spectrum of the “unknown” element could be calculated from Moseley’s law. But none of the specimens revealed any spectral features even remotely indicative

of the element No. 61. The two German chemists made some far-reaching conclusions from their failure which we find highly instructive. They wrote: "That a systematic search has not revealed any traces of the element No. 61 has a noteworthy and hardly accidental cause. It can be concluded that the element No. 61 differs from the rare-earth metals in its chemical behaviour or that it does not exist at all."

But Prandtl and Grimm were tempted to make even more "far-reaching" conclusions and generalizations. Figure 17 shows a fragment of the periodic system in their representation. All the elements in Group 7, except for manganese, are unknown. They suggested that "...The empty slots Nos. 43, 61, 75 and 93 could be a manifestation of some periodic regularity and that it was possible that they would never be filled."

Bohr's theory of atomic structure wrote off the assumption about the unprecedented chemical originality of the element No. 61 showing that it could not be markedly different from other rare-earth elements.

What remained was the hypothesis about the extreme rarity or even complete absence of the element No. 61. Such a hypothesis could neither be proved nor disproved. Nobody paid any attention to the chance remark made by the chemist Ida Noddack about possible radioactivity of "eka-neodymium".

Nothing chemists did could entice the element No. 61 from its hiding.

Things started happening in 1926.

The first face: illinium, II. Now is the time to tell the story of illinium in more detail than we did a few pages earlier.

For the first time the New World could claim the honour of the discovery of a new element. The

discovery was not unexpected—it took long years of careful work to prepare for it. The US Bureau of Standards started wide-ranging spectral studies of the rare-earth elements back in 1919. The chemists from the University of Illinois took part in these studies. A large spectral atlas was compiled for lanthanum and lanthanides. Several of the spectral lines in it could not be properly identified and some scientists were tempted to assign these lines to the unknown “eka-neodymium”.

The temptation gradually gave way to a firm conviction. X-ray spectroscopic studies were performed in addition to optical spectroscopy. The chemist Intema conducted repeatedly fractional recrystallization and prepared specimens which he believed to contain the element No. 61 together with neodymium and samarium. Harris and Hopkins recorded the spectra of the specimens and analyzed them.

These joint efforts led to the success.

Actually, it was a qualified success as the new element was identified by its spectrum but was not obtained in the material form. The American scientists failed to prepare even a tiny amount of any of its compounds, say, Il_2O_3 .

However, the symbol Il appeared in the slot No. 61 of the periodic system and on the pages of the chemical textbooks (it could still be found in some books published as late as the middle of the forties).

It would not be at all unusual if only the discovery of illinium could have been repeated.

But the fact was that nobody could do that. Prandtl severely criticized the conclusions made by the American scientists. The grand old man of the rare-earth chemistry von Welsbach voiced his serious misgivings. Finally, Ida and Walter Noddack, the German husband-and-wife team, pulled illinium apart.

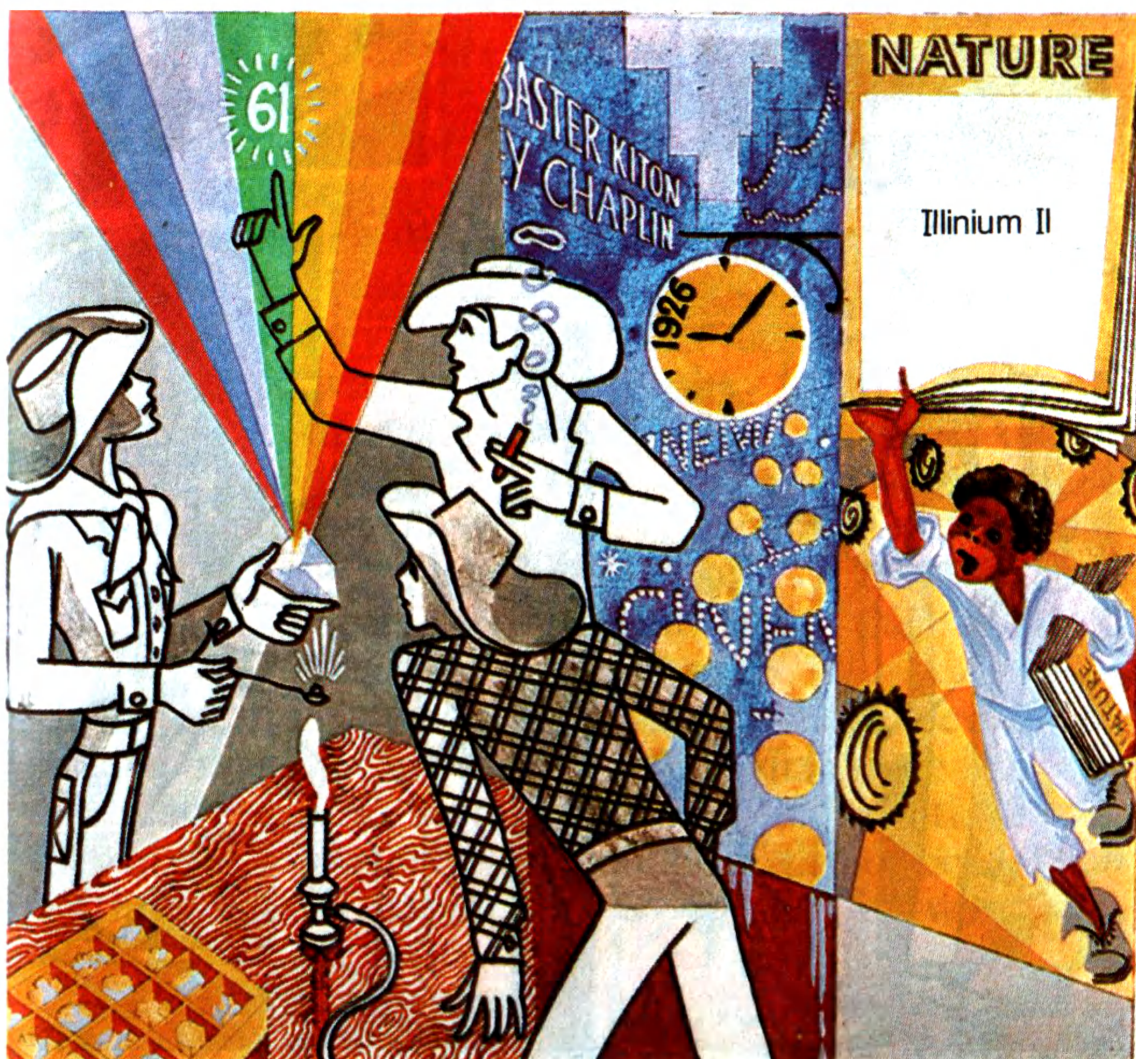


Fig. 18

The Noddacks carefully processed tens of kilograms of the rare-earth minerals and obtained specimens of pure neodymium and samarium. They conducted exhaustive X-ray spectroscopic studies and repeated all procedures performed by Harris, Intema and Hopkins. All the results were negative. The Noddacks declared: "Even if the element No. 61 were ten million times more rare than neodymium and samarium our studies would allow us to find it."

But it was not found.



Fig. 19

The second face: florentium, Fl. Soon after the scientific community had learned about the discovery of illinium from the pages of *Nature* other scientists claimed the priority of its discovery.

At the very beginning of 1927 two Italian scientists, Luigi Rolla and Luigi Fernandes, who worked at the University of Florence, published a paper under the heading “Illinium or florentium?”. One can easily guess that their chosen name for “eka-neodymium” (whose discovery they claimed) was florentium rather than illinium.

It was not the first time in the history of elements that claims of discoveries had clashed. But there was a touch of a second-rate mystery about the florentium claim. The Italian scientists told a bizarre story. Allegedly, they had proved the existence of the element No. 61 with various methods back in 1924. Later they described their discoveries in two lengthy papers which, however, they did not intend to publish at the moment. Instead, they took the mystifying step of storing these papers “in a sealed envelope” with the renowned Academia dei Lincei in Rome. What was the aim of the scientists from Florence? Why did they want to keep their alleged “discovery” in secret for a time?

These questions remained unanswered. However, the dispute about priorities did not materialize since illinium was already under pressing attack. In addition, the mysterious circumstances surrounding the discovery of florentium did a disservice to it as it was just ignored.

Ida Noddack sadly summarized the situation in the following words: “We are facing a mystery—an element is missing in the group of trivalent rare-earth elements whose abundances follow a generally regular pattern and whose electronic structure is well known.”

Three explanations and their relative contributions. When the controversy about illinium subsided the scientific community became quiet on the subject. But it was a quietness of bewilderment; scientists just did not know what to do next.

The empty slot between neodymium and samarium served as a continuing reproach to chemists and the chimerical symbol of illinium, Il, just emphasized the emptiness. But the force of habit proves sometimes

excessively strong and the name given by the American “discoverers” still lingered in the pages of scientific publications. In fact, it was quite commonly used until the end of the twenties.

We shall use it too so that not to use the awkward term “the element No. 61”. Thus, how could the scientists explain the amazing elusiveness of illinium? There were three more or less plausible explanations.

According to the geochemical explanation, illinium was so rare that it could not be found even with the most sensitive X-ray spectroscopic analytical techniques. But it was in the twenties that the Soviet geochemists Vernadsky and Fersman demonstrated that the abundance of the rare earths on Earth was sufficiently high so that the adjective “rare” could not, in fact, be properly applied to them. Then why could illinium be an exception among other rare-earth elements? No reasons for that could be found.

Thus the first explanation can be dismissed.

According to the second, chemical explanation, illinium was a “freak” in the rare-earth family. This is shown to be untrue on pp. 94-95.

The third explanation was particularly decisive. According to it, illinium just did not exist in nature. Of course, it was not chemists’ business to work on such a hypothesis.

But what do we mean by saying that it does not exist in nature? Or did it never exist? These two questions lead to the third question—maybe, illinium did exist in the past? Suppose it was a highly radioactive element with a short lifetime so that it just decayed by our time and transformed into other stable elements....

Radioactive illinium? Since the discovery of radioactivity at the end of the last century scientists used to think that only the heaviest elements in the

periodic system could be radioactive. Illinium was placed not very far from the end of the periodic system but still too close to its centre. It is true that a sensational finding was made in 1906 – potassium and rubidium (much lighter elements than illinium) were observed to produce very weak emissions of electrons, that is, the beta rays as they are known now. They were so extremely weak that many scientists expressed grave doubt about their existence saying that they were due to experimental errors. Later they were proved to be a fact.

Still, we shall refer to the third explanation as the radioactive hypothesis.

Astonishingly, it was this explanation that was ultimately shown to be true.

A few elementary truths. According to the modern concepts, isotopes are the varieties of atoms of a chemical element which contain in their nuclei identical numbers of protons and different numbers of neutrons. For instance, the natural isotopes of oxygen ($Z = 8$) contain 8, 9 or 10 neutrons in their nuclei and are denoted by the symbols ^{16}O , ^{17}O and ^{18}O , respectively. The superscript to the left of the symbol is the mass number of the isotope which is the sum of the numbers of protons and neutrons.

Isotopy was first found for the radioactive elements located at the end of the periodic system (it was defined by the English physicist Frederick Soddy in December of 1913) and later for stable elements. Great contribution to these studies was made by other English physicists, Joseph Thomson and particularly his student Francis Aston.

By the end of the twenties isotopes had been found for many stable elements including almost all rare-earth elements.

Another concept of nuclear physics which is relevant to our story is that of isobars. Isobars are atoms of different elements which have different numbers of protons (Z) and neutrons (N) but the same mass numbers ($Z + N$). For instance, ^{40}K (with 19 protons and 21 neutrons) and ^{40}Ar (with 18 protons and 22 neutrons) are isobars.

The science that classifies isotopes is known under the rather dull-sounding name of isotope statistics. But it was this apparently unexciting science that resolved the baffling problem of illinium and demonstrated the correctness of the radioactive hypothesis.

The Mattauch rule. Now we shall do what is often done in school textbooks, on mathematics where a theorem is first formulated and then proved. So we shall first formulate the rule.

If the nuclear charges of two isobars differ by unity one of the isobars must be radioactive.

For instance, take the two isobars we have mentioned above— ^{40}K and ^{40}Ar . Their nuclear charges (the atomic numbers) differ by unity and potassium-40 is known to be radioactive.

This rule was put forward by the German theoretical physicist Josef Mattauch in 1934 after he had analyzed and compared all the data about all isotopes known at the time. In fact, a similar idea was suggested in the middle of the twenties by the Soviet chemist Sergei Shchukarev, but too few isotopes of stable elements were known at the time to substantiate it.

The rule as formulated by Mattauch gave only a quantitative description of the properties of isobars. It was proved rigorously by theoretical nuclear physics at a much later date. We shall not go into the details of it as it is well outside the scope of this book. So, we shall take this rule for granted.

Now let us substantiate the radioactive hypothesis using this rule.

Write down the mass numbers of the natural isotopes of neodymium and samarium.

The mass numbers of the neodymium isotopes are

142 143 144 145 146 — 148 — 150

The mass numbers of the samarium isotopes are

— — 144 — — 147 148 149 150

The mass numbers of the illinium isotopes if they exist must be in the range from 142 to 150. But it is precisely these mass numbers that have already been “used up” by the stable isotopes of neodymium and samarium. Hence, illinium cannot have stable isotopes, its isotopes must be radioactive.

This conclusion finally explained the failure of the search for the element No. 61 in nature carried out for many years.

However, the Mattauch rule does not show how unstable the illinium isotopes are. For instance, the natural isotopes of uranium and thorium are also radioactive but their lifetimes are quite long and therefore their abundance on Earth is quite substantial.

Perhaps, illinium has at least one long-lived isotope which still has not decayed since the birth of our planet?

In short, the Mattauch rule calmed some hotheads but did not rule out the search for illinium in nature. Occasionally successful results of such searches were reported but nobody paid much attention to them. Their worth has been well known since the illinium discussion of the twenties.

The American physicist Willard Libby, the future Nobel prize-winner, made an interesting finding the same year, 1934. He discovered what apparently was

a weak beta-ray activity of neodymium, illinium's neighbour on the left. But since neodymium emitted beta particles then, according to the well-established Soddy's displacement law, it could convert into nothing else but illinium. As radium is a decay product of natural uranium, illinium would be a daughter product of neodymium. This was yet another reason for continuing the search for illinium in the natural minerals.

In fact, the element No. 61 was after all found in nature. But this is quite another story. Scientists got their first glimpse of this element under entirely different circumstances.

The third face: cyclonium, Cy. "If an element does not exist in nature it must be made artificially." This motto may have sounded utterly fantastic in the twenties but it had become realistic by the end of the thirties.

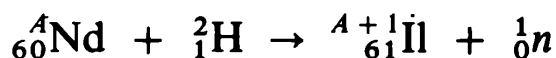
By that time scientists had learned how to perform nuclear reactions. They could do that with a variety of bombarding particles, namely, alpha particles, protons, neutrons and deuterons (the nuclei of the heavy hydrogen isotope, deuterium). To penetrate the nucleus of the target element the charged bombarding particle had to have a high energy. Special accelerating machines, cyclotrons, were built to produce such high-energy particles.

The first artificially produced chemical element was technetium which has the number 43 in the periodic system (incidentally, it also does not have stable isotopes according to the Mattauch rule). Technetium was produced in 1937 and chemists managed to analyze its chemical properties (it is an analogue of manganese), though they had in their disposal as little

as one ten-billionth of a gram of the new element. The advances of physics in the synthesis of artificial elements made chemists develop new sophisticated techniques for working with negligible concentrations of them.

The turn of the element No. 61 apparently came in 1938. In July of that year the American physicists Marion Pool and Laurence Quill from the University of Ohio bombarded a neodymium target with fast deuterons.

They used as a target a naturally occurring mixture of the neodymium isotopes. The equation of the nuclear reaction with a given isotope could be written as



This means that the reaction produced an isotope of illinium and neutron.

The long-awaited illinium was synthesized in such tiny quantities that it was hardly possible to study its properties. Nevertheless, Pool and Quill made the conclusion that they had produced the illinium isotope with the mass number 144 which exhibited beta-ray activity and had a half-life of 12.5 hours. Thus, the first-born was short-lived.

Two years later the determined scientists with the assistance of George Kurbatoff and Henri Low repeated their experiments on a much larger scale. Now they reported synthesis of three isotopes with the mass numbers 144, 147 and 149.

This apparently significant and impressive success gave the scientists the right to suggest the name for the new element. Pool and his co-workers did not hesitate to use this right. The name illinium was to give way to cyclonium which was chosen to emphasize the essential part played by cyclotron in the discovery of this element.

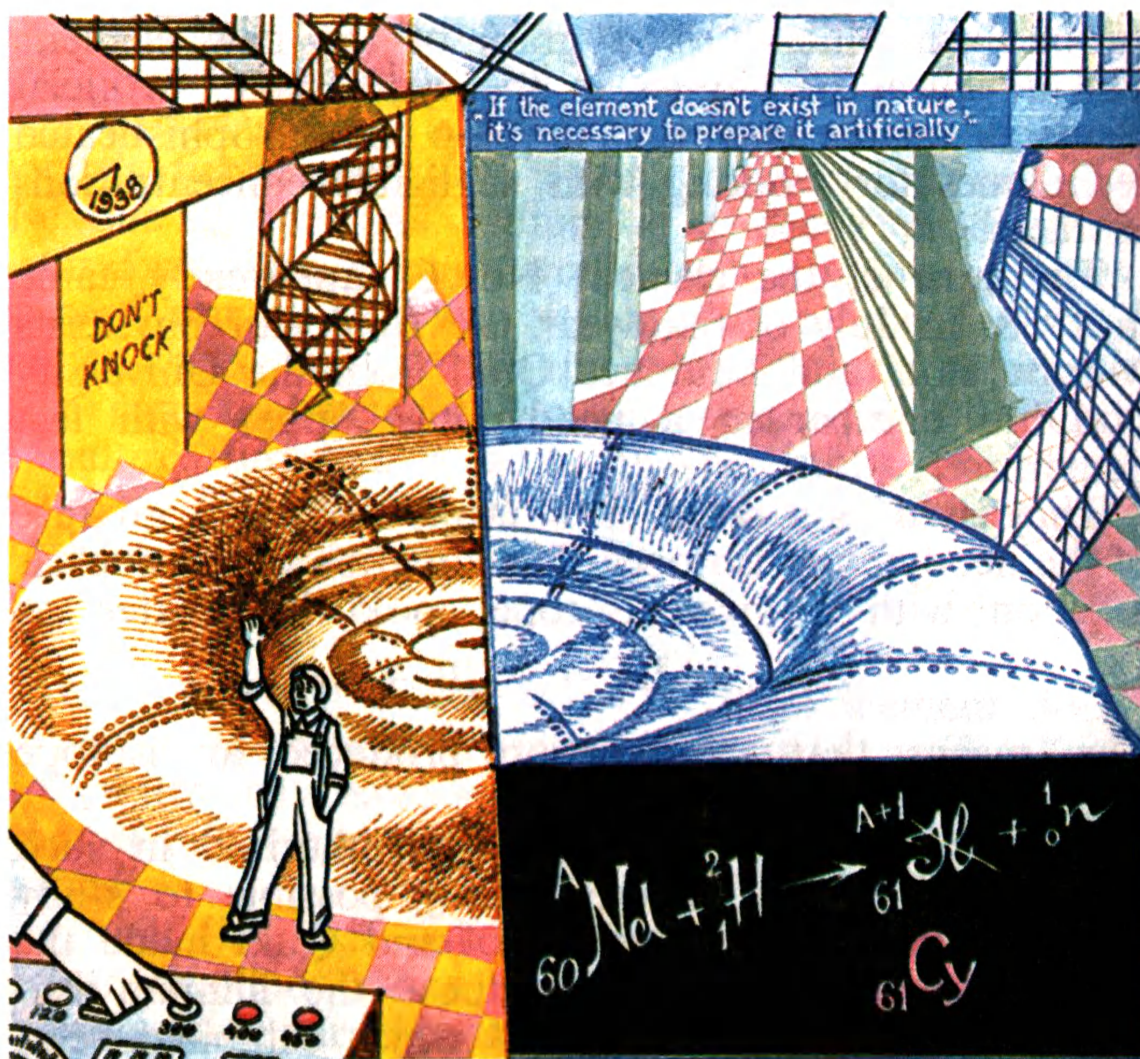


Fig. 20

But now let us make some comparisons.

When technetium was synthesized the determination of its chemical nature and the properties of its isotopes raised no doubts though it was only much later that scientists could prepare it in visible amounts.

In 1940 another empty slot was filled in the periodic table, the element No. 85, the heaviest halogen, was synthesized and named astatine (At). Though astatine proved to be the second shortest-lived element among all naturally occurring elements (after francium, No. 87) nobody had any doubts about it, too.

But scientists did raise questions about cyclonium. They did not believe that the neodymium targets were sufficiently pure because even at the end of the thirties it still was very difficult to produce pure rare-earth metals. The impurities in the target material could be involved in nuclear reactions so that isotopes of other lanthanides could be produced instead of (or together with) the isotopes of cyclonium. It introduced a high degree of uncertainty into the results. As in the past chemists had worked with intricate mixtures of the rare-earth elements, this time they had before them a maze of artificial isotopes. Chemical extraction of cyclonium was just unthinkable and this gave yet another reason for considered skepticism.

In short, the synthesis of cyclonium could not be regarded as a definite success. We still do not know whether the scientists from Ohio did really produce the element No. 61. As a consequence, the name cyclonium did not live on as the final name of this element.

Again the nuclear ABC. The development of nuclear physics was greatly accelerated in 1932 by the discovery of the neutron—the elementary particle which had no charge and was a component of atomic nuclei.

Since the neutron was an electrically neutral particle it could easily penetrate any atomic nucleus. This opened a highly promising way for artificial synthesis of new isotopes and elements.

Targets made of various elements were bombarded with neutrons. Soon the turn of uranium came. What happens when a neutron penetrates the nucleus of ^{238}U ? The reaction product is a new uranium isotope with the mass number 239 which does not occur naturally. It emits beta rays giving rise to an isotope of the first transuranium element No. 93.

Such was the reasoning of the great Italian physicist Enrico Fermi and his co-workers when they bombarded uranium targets with neutrons. Their ideas were supported by many other scientists. The reaction products were frequently found to contain unknown isotopes which they believed to be isotopes of the transuranium elements Nos. 93, 94, 95 and so on.

But there was a single dissenting voice hardly heard against this chorus of agreement. Ida Noddack made a suggestion that sounded quite heretical (at the time). She said that the uranium nucleus could be split by a neutron into two fragments that could be the nuclei of elements belonging to the central part of the periodic system.

Another prominent German physical chemist, Otto Hahn, just smiled condescendingly on learning about this suggestion.

But now you can read in any textbook on nuclear physics that Otto Hahn was wrong and Ida Noddack was right. In fact, it was the very same Hahn who found the experimental proof of this idea with his student Fritz Strassman in December of 1938.

That was the discovery of fission of uranium nuclei under irradiation with neutrons. The fission fragments included the nuclei of elements from the central part of the periodic system and among them isotopes of many rare-earth elements.

Therefore, this conglomerate of radioactive nuclei could contain the isotopes of the elusive element No. 61 known variously as illinium, florentium and cyclonium.

The fourth-true-face: promethium, Pm. In 1942 the US government started a wide-ranging research and development programme known as the Manhattan Project. Its goal was the development of nuclear

weapons. Many hundreds of experimental and theoretical physicists and chemists, engineers and technicians took part in this project. Among the problems to be solved was the physical and chemical determination of the products of uranium fission including the isotopes of the rare-earth elements.

Now once again the emphasis was on the chemical studies. Chemists had to develop new techniques for separating isotopes of the rare-earth elements.

Ion exchange chromatography was successfully applied for this purpose. In this technique special high polymers, ion exchange resins, are used for separating the rare-earth elements.

At the end of 1945 the American chemists Jacob Marinsky, Lawrence Glendenin and Charles Coryell performed an extremely careful chromatographic separation of a mixture of lanthanide isotopes produced by uranium fission. They managed to isolate from this mixture traces of the element No. 61 (they obtained five-millionth of a gram of the new element; this amount was a thousand times greater than the amount of technetium produced for the first time). They reliably identified two isotopes with the mass numbers 147 and 149; the first of them had a half-life of over three years which was quite a long time in comparison with some other isotopes radiochemists had to study.

In 1947 the discoverers suggested the name promethium for the element No. 61 for the mythical hero Prometheus who stole fire from heaven, gave it to man and was consequently tortured by Zeus for that. To justify their choice of the name they wrote (in somewhat stilted language) that it symbolized not only the dramatic way in which the new element was obtained in noticeable amounts as man mastered the energy of nuclear fission but also the impending danger posed by the eagle of war.



Fig. 21

Those participating in the session of the American Chemical Society on July 28, 1948 could see with their own eyes the compounds of promethium—three-milligram specimens of its chloride and nitrate.

Twenty years later negligible concentrations of promethium were found in a naturally occurring mineral, namely, in pitchblende. It is produced there in the course of spontaneous fission of uranium.

Thus ends the story of the long search for the element No. 61. It had to be produced artificially

before being found on Earth.

Now scientists could start studying it.

Promethium today. Before closing the subject of the “missing rare-earth element” let us look more closely at what is known about it now.

Promethium has the same chemical properties as other lanthanides, it is just as persistently trivalent in its compounds.

In 1963 promethium was for the first time obtained in the metallic form. Just as other rare-earth metals it can be said to have the “middle-of-the-road” properties.

But the nuclear properties of promethium exhibit some interesting features.

The longest-lived promethium isotope, the beta-ray active ^{145}Pm , has a half-life of 18 years.

A theoretical prediction was made that it could also exhibit alpha-ray activity and that the corresponding life-time should be more than a thousand billion years. Later this prediction was verified by experiments. Thus it was found that ^{145}Pm was the lightest alpha-ray isotope among all the known isotopes.

But can we say now that nothing mysterious is left about the element No. 61, that it will not give rise to any new riddles? No, we cannot. The most amazing of lanthanides has perhaps many more surprises for scientists who have not yet emptied the entire contents of the “sealed envelope”.

A Coming Age of Rare-Earth Elements?

Looking around us we may come to the rather obvious conclusion that the modern civilization is built, so to say, on a metal foundation. It is the metal

(in a wider sense) that penetrates the outer space and the ocean deeps, builds houses and tills the fields, and transports loads and men over great distance. Metals are used everywhere.

About 70 metals naturally occur on Earth and a quarter of them are the rare-earth elements. The figure emphasizes the enormous potential of this group of metals.

But it was only recently that man started to tap this potential. The years after the Second World War saw the beginning of a scientific and technological revolution that developed on a scale unprecedented in the history of human society. The demands of the revolution stimulated production of new materials with unheard-of properties while old well-known materials and substances found new astonishing applications. New uses were found for practically all elements from the periodic table. The progress in the applications of the rare-earth elements was particularly significant.

It was less than a hundred years ago that the astute Austrian von Welsbach found the first practical application for the rare-earth elements. His gas mantle illuminated the beginning of the history of the rare-earth utilization which went the whole way from primitive flints for lighters up to sophisticated materials used in supersonic planes and space vehicles.

Rare earths in steels and alloys. Manufacturing of high-quality steel is a very complicated process. To conduct it properly one needs considerable experience in metallurgy and good knowledge of the properties and behaviour of metals.

The properties of steels are greatly affected by impurities in it. Negligible impurities of oxygen, sulphur,

nitrogen or phosphorus can sometimes result in a significant deterioration in the quality of steel. It can become brittle and its durability and heat resistance can deteriorate. Therefore, such harmful impurities must be removed in the process of steel smelting.

It is done by adding special substances for degassing, desulphurization and deoxidizing. Thus, the harmful "poison" is removed from steel.

Traditionally, highly reactive metals were used for this important purpose. For instance, the alkali metals are very good for desulphurization. Unfortunately, their boiling points are too low and the losses of these valuable metals are too high.

This is where the rare-earth metals came to assistance of steelproducers. They proved to have a very valuable property, namely, that they have high boiling points while being highly reactive (particularly, with respect to oxygen, nitrogen and sulphur). This means that, firstly, the rare-earth metals can successfully act as cleansing agents removing the "poisons" from steel and, secondly, they can easily be alloyed with many high-melting metals.

The rare-earth metals in combination with other metals can produce a wide variety of alloys some of which can have quite unexpected and unusual properties.

The alloys of the rare-earth metals are still mostly at the stage of research and development, though some of them have already been applied in industry. For instance, the samarium-cobalt alloy, SmCo_5 , is a perfect material for permanent magnets. Some alloys of dysprosium exhibit magnetic properties only at very low temperatures.

But what is mostly used now is not the individual rare-earth metals but their mixtures. The most widely used one is the so-called mish metal which contains

60-65% of cerium. Another widely used mixture is that of iron and cerium known as ferrocerium.

The properties of a steel can be sharply improved by adding mish metal in a concentration of the order of 0.1%. Sulphur and gases are removed from the steel and it becomes more ductile and easier to work. The plasticity of the steel improves sharply in a wide temperature range and the resistance to heat and corrosion is markedly increased.

The chemically resistant stainless steels are indispensable for the present-day technology. Such steels contain high concentrations of nickel and chromium. Though the addition of these metals gives rise to a wide variety of valuable properties in steels it also produces some drawbacks. The chrome-nickel steels are difficult to roll and their machining leads to a considerable wastage of the metal. The addition of mere 0.03% of mish metal to such steels produces a veritably miraculous effect. The plasticity of steels is sharply improved so that they become much easier to roll and machine and the wastage of the metal is practically eliminated.

The advantages of the use of the rare-earth metals in steelmaking can hardly be overestimated. In fact, scientists claim that the application of the rare-earth elements was the single greatest achievement in steel-making in the last several decades.

Many alloys of lanthanides with various ferrous and nonferrous metals exhibit highly useful properties.

Cerium and iron form pyrophoric alloys tiny particles of which ignite spontaneously in air.

Special surgical instruments are made with steel containing 6% of rare-earth metals.

An alloy of cerium, iron and manganese has a very low thermal expansion coefficient; it is successfully used for manufacturing critical components of internal combustion engines. The aluminium-cerium alloys have

similar properties; they are well known in the aircraft industry.

The rare-earth metals proved to be excellent companions of magnesium. The light and strong (stronger than many steels) magnesium alloys contributed to many new technological advances. Unfortunately, their heat resistance is poor and their properties deteriorate at temperatures just above 100°C . But the addition of the light rare-earth metals—lanthanum, cerium, neodymium and praseodymium—largely eliminates this drawback. These alloys retain their properties at temperatures up to 350°C and their corrosion resistance is much higher.

The heat-resistant alloys of magnesium with lanthanides are used for manufacturing components of supersonic aircraft, guided missiles and shells of the spacecraft.

It would not be an exaggeration to say that the use of lanthanides will bring about a veritable revolution in metallurgy. The main problem here is to find methods for fast and cheap production of large amount of pure rare-earth metals.

One may recall that the large-scale use of aluminium was started only after a comparatively cheap method for its production had been found. The same will possibly happen with the rare-earth metals.

Rare earths in glass. The beautiful transparent mineral alexandrite is very rarely found in nature. It has one amazing property—it shows different colours in the daylight and in the evening light. But if we add quite a small amount of the oxides of neodymium and praseodymium to the molten normal glass it acquires the same property.

Glassmakers had used rare earths for colouring glass from ancient times even before Gadolin extracted a

mixture of yttrium “earths” from ytterbite. It was just known that coloured glass could be produced by adding certain minerals (which later were found to contain rare earths).

Now a wide variety of processes and recipes are available for producing glass of any colour without the addition of the oxides of the rare-earth elements. Nevertheless, they still have a major role to play in modern glassmaking.

Most types of glass utilized in industry and in households, useful as they are, have one significant drawback. They lose transparency and become clouded with time. The reason is that these glasses contain iron in the divalent state which leads to the decrease in transparency with time.

But if we transform iron from the divalent state to the trivalent state the transparency of the glass increases almost ten times. To this end oxidizers (typically, the oxides of arsenic or antimony) are widely used in glassmaking. The oxidizers “make” the iron trivalent.

But though these additives eliminate one fault they give rise to another—bubbles and ripples appear in the glass batch. They are caused by the oxygen which is liberated when the oxides of arsenic and antimony oxidize iron. In addition, the glasses that contain arsenic grow yellow under the effect of the sunlight and are clouded under the effect of X-rays.

These faults are often very difficult to eliminate.

It was cerium that came to assistance of glassmakers. Very small amounts of cerium dioxide added to glass miraculously remove cloudiness and make the glass stably transparent so that even prolonged irradiation with hard rays does not harm it.

The rare-earth elements are highly useful for manufacturing special glass. The addition of lanthanum and boron makes it possible to produce glass with a very

high index of refraction. The optical glass for high-precision spectroscopic and astronomic instruments is obtained by adding neodymium in combination with vanadium. Lanthanum and lithium impart to glass high electrical conductivity while the addition of silver and cerium sharply increases the light sensitivity of glass.

Glass polishing is an important procedure in manufacture of glass. Conventional polishing with oxides of such metals as iron, zinc, chromium and nickel takes a long time. A new widely used abrasive containing 90-95% of rare earths is twice as effective as the conventional preparations.

The rare earths help to conquer the atom. Imagine that man had understood in principle how to liberate the nuclear energy much earlier than it actually happened, say, 50 years ago. Could it be possible to build nuclear power stations and nuclear-powered ships at the time?

Of course, it could not. It is not enough just to know the principle of a thing. Much was needed to realize the controlled nuclear reaction. First of all, scientists needed special materials to build nuclear reactors and such materials were developed only as a result of sustained hard efforts.

Let us take just one example. One can say that the controlled reaction taking place in a nuclear reactor is within an ace of the nuclear explosion. When the concentration of free neutrons exceeds the critical value instantaneous fission of the entire nuclear fuel occurs. To prevent it special safety devices are needed. These are the control rods that absorb the excess neutrons. Of course, such rods can be made only with the materials that readily capture neutrons. But only few materials proved to have such properties. They are boron and cadmium which are widely used for manufacturing the

control rods for reactors. Now it is known that three of the rare-earth metals, namely, samarium, europium and gadolinium possess an amazing capacity for absorbing neutrons. In fact, samarium and europium have a neutron-absorbing capacity that is 1.5-2 times higher than that of boron while gadolinium is ten times more efficient than them.

The lanthanide-containing rods are now used as highly effective tools for controlling the operation of nuclear reactors.

Lanthanides are also added to the refractory and ceramic materials used in nuclear reactors. Protective goggles for personnel working at nuclear installations are made with glass containing neodymium which absorbs neutron radiation.

Another field in which the rare-earth elements proved to be of great assistance to scientists is the processing of nuclear fuel.

The end products of some uranium nuclear reactors contain plutonium which is an excellent nuclear fuel in its turn. Uranium and plutonium are similar in their properties and it is not easy to separate them chemically. The conventional separation technique is based on the difference in stabilities of the different valence states of uranium and plutonium (hexavalent uranium and tetravalent plutonium are stable). But tetravalent plutonium proved to be similar to lanthanum. Therefore, if we add lanthanum fluoride LaF_3 to a solution containing salts of U^{6+} and Pu^{4+} almost all plutonium is precipitated together with lanthanum while uranium remains in the solution. The process is repeated several times to provide for complete separation of uranium and plutonium.

Another process for extracting plutonium from uranium is based on the fact that the solubility of plutonium in the rare-earth metals is much higher

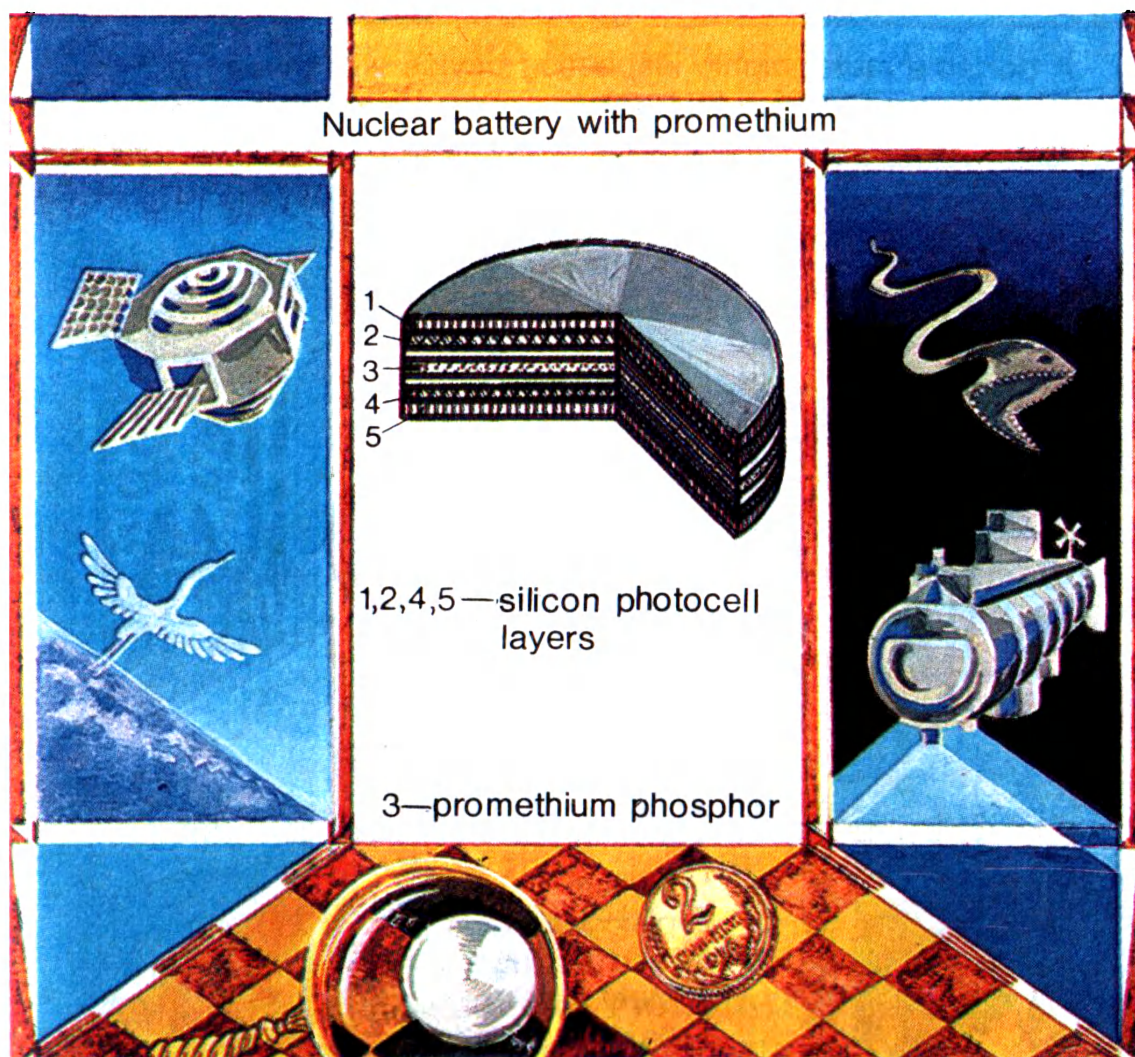


Fig. 22

than the solubility of uranium. Plutonium is separated from molten uranium by adding to it molten lanthanum, cerium and neodymium.

The rare-earth elements also feature prominently among the radioactive isotopes used for peaceful purposes.

About 150 radioactive isotopes of lanthanides have been synthesized by scientists. At least 20 of them have found various uses in science and technology. The most widely used isotopes are promethium-147 and thulium-170.

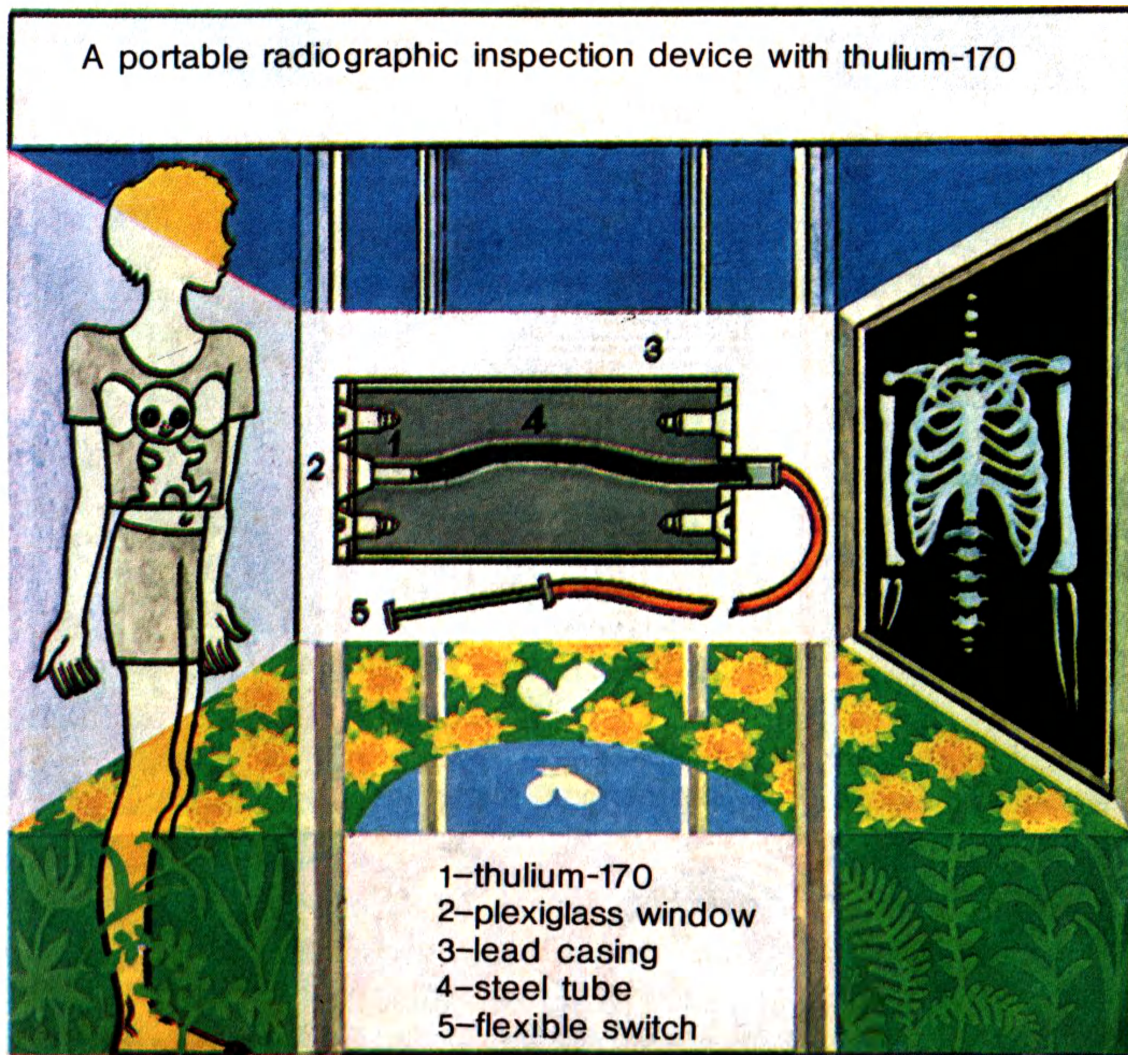


Fig. 23

Promethium serves as a source of radiation in nuclear batteries. It has many advantages in comparison with other radioactive isotopes (not only isotopes of lanthanides). It has a comparatively long half-life (2.7 years) and produces soft (low-energy) beta rays. No complicated safety precautions are needed to handle it.

Figure 22 shows schematically a nuclear battery with promethium-147. It is a thumbtack-sized disk with a thickness of about 1 mm. Its principle of operation is simple—the energy of the beta particles emitted by the

isotope is converted into the light energy and then the light energy is converted into the electrical energy by photocells. The light source (3 in Fig. 22) consists of a mixture of finely divided phosphor and promethium oxide (about 5mg). The phosphor absorbs beta particles and emits light which is converted by photocells (1, 2, 4 and 5 in Fig. 22) into electric current. The battery operates in a very wide temperature range for up to five years. It can be used for a variety of applications.

The devices employing thulium-170 are starting to compete with medical X-ray apparatus. The gamma rays emitted by thulium make it possible to examine all parts of the human body. Specially trained personnel and electric power supply are needed to operate the complicated X-ray equipment while the thulium medical devices are incomparably simpler to handle. They have a simple design, low weight (not more than 20 kg) and small size and do not require a power supply. They are indispensable under the field conditions.

The gamma radiation of thulium-170 is widely used for industrial radiographic inspection of various metal components to find imperfections in them.

Once archeologists found an ancient Assyrian helmet. They could not inspect it with a conventional X-ray apparatus because it had a spherical shape. However, they examined it with a thulium-170 device and discovered inscriptions and symbols on it.

Europium-155 and cerium-144 are also used for radiographic inspection. They have proved to be indispensable for quality control.

Radioactive isotopes of almost all lanthanides are employed as tracers in the studies of various chemical reactions.

The omnipresent elements. We have already told about the major applications of lanthanides. Where else can we meet them?

What we discussed above was the use of lanthanides in the new fields of science and technology but they find application in old well-established industries, too.

Take, for instance, the chemical industry. The problems of catalysis are of major importance for it. Thousands and tens of thousands of catalysts have been found by scientists to promote various chemical processes. The rare-earth metals and their compounds feature prominently among them.

The compounds of cerium are particularly important as catalysts. For instance, CeO_2 catalyzes the reaction of carbon monoxide with hydrogen which plays a very important part in the production of many valuable compounds. The cerium ions catalyze the production of quinone from aniline. Cerium sulphate serves as a good catalyst for the oxidation of sulphurous-acid anhydride to sulphuric anhydride. Cerium oxide is a catalyst for the production of acetic acid. Oxides and salts of lanthanum and praseodymium are also put to work as catalysts. For instance, Pr_2O_3 catalyzes the oxidation of ammonia at low temperatures and lanthanum manganate catalyzes the oxidation of carbon monoxide.

Some compounds of lanthanides are highly effective in promoting the effect of other catalysts when they are added to them. For instance, the addition of 10% La_2O_3 to the magnesium-silicon ($\text{MgO} + \text{SiO}_2$) catalyst results in a two-fold increase in the yield of the hydrocarbon octane during processing of oil.

But the prospects for future progress in lanthanide catalysis are even more wide-ranging.

Now, if we turn to quite a different industry—electrical engineering and radio electronics—we can see that the rare-earth elements prove to be of great service there, too. Fluorides of cerium and lanthanum are added to the material from which the electrodes of the arc lamps are manufactured. Lanthanides are highly useful for absorbing the residual gas in electron vacuum tubes. Special ceramics used in electronics contain the rare-earth metals among other components.

We have surveyed only a few fields of human activity. If we had looked at many other fields, say, medicine, agriculture, food industries, etc., everywhere we would have seen the rare-earth elements making valuable contributions.

The future of rare earths. We have started this chapter with the question about a coming age of the rare-earth elements.

It has long been a custom to refer some periods in human history to the progress in some field of knowledge or the use of a particular material. For instance, the 20th century has been called the age of steel, the age of electronics, the age of aluminium or the age of titanium and each of these names can be supported by evidence.

So how about the rare-earth elements?

It can be said that their time has come but their age is just dawning. The “rare-earth continent” has been mapped fairly well but the significant features of the terrain are yet to be studied. That is to say that we know too little about the distinguishing properties of the individual rare-earth metals and about their capabilities. To find out everything about them is the primary aim of the current rare-earth work.



Fig. 24



Fig. 25

Though the abundance of the rare-earth elements on Earth is comparatively high they still are very expensive to produce. The cost of extracting some lanthanides in pure form is a few times that of extracting gold. Their use is of course limited by their cost. Chemists must develop new efficient techniques for extracting and separating lanthanides and for preparing them in the metallic form.

In Conclusion: Are There “Relatives” of Rare-Earth Elements?

First, let us define the meaning of “relatives” as applied to elements in the periodic system.

Talking in terms of the electron shells we can classify all the known chemical elements into four sets.

The first set is that of the *s* elements for which the quantum number *l* is zero (see pp. 46-55). It includes hydrogen, helium, the alkali and the alkaline-earth metals.

The second set includes the *p* elements ($l = 1$) belonging together with the *s* elements to the subgroups A of the periodic system. It contains metals and nonmetals.

The third set includes the *d* elements ($l = 2$); they are all metals and belong to the subgroups B of the system.

Finally, the fourth set consists of the elements which are the subject of this book, the *f* elements ($l = 3$). They have the atomic numbers from 58 to 71.

Now, the *s* elements have “relatives” in all periods of the periodic table. Each period starts with *s* elements. The *p* elements are also found in all periods except the first period. The *d* elements appear only in the long periods of the system starting from the fourth

period. This distribution of “relatives”, as we have mentioned above, is an important structural feature of the periodic system.

The *s* elements are, so to say, a “well-disciplined” family. All the *s* elements belonging to different periods exhibit considerable similarity in their chemical behaviour. The only exceptions are the gaseous elements, hydrogen and helium, belonging to the first period. But they are, of course, the very first elements in the system and have the simplest atomic structures.

In comparison, the *p* elements belonging to different periods have markedly different properties. In fact, this family of elements exhibits a greater diversity of properties than other families in the periodic system. This is not accidental but a consequence of their atomic structure. The greater similarity between the metallic *d* elements is also explained by the peculiar features of their atomic structure.

Thus, we have identified seven “families” of the *s* elements, five “families” of the *p* elements and three “families” of the *d* elements in the periodic system. But in the sixth period we come upon a seemingly unique family of chemical analogues—the *f* elements. Then what we know about the structure of the periodic system leads us to the conclusion that the next period, the seventh, must contain a related family of elements—the *5f* elements.

In fact, this is an obvious conclusion. The table of elements shown on pp. 52-53 of this book contains this series of the *5f* elements, known as actinides, under the lanthanide series. It starts with thorium (No. 90) and ends with lawrencium (No. 103). The series has 14 elements just as the lanthanide series.

So the question heading this section can be answered very simply—the *4f* elements in the sixth period have

“relatives” in the seventh period, namely, the $5f$ elements. However, this simplicity is deceptive... .

Simplicity is not always so simple. When Bohr worked on his theory of the periodic system he was convinced that, in accordance with the laws of atomic structure, the seventh period had to contain the second “rare-earth series”. The only thing he could not know for certain was which element had to be the first in this series.

“Of course, thorium!” –would jump to a hasty conclusion some readers. As the $4f$ elements appear after lanthanum, the $5f$ elements should follow actinium which is the analogue of lanthanum in the seventh period.

But at the time Bohr formulated his theory the periodic system ended with uranium. The number of known elements in the seventh period was too small. But, if we follow the reasoning of the hasty readers, three of them –thorium, protactinium and uranium –had to belong to the $5f$ elements. The consequences of it had to be such:

- thorium had to be similar to cerium, protactinium to praseodymium and uranium to neodymium;

- thorium, protactinium and uranium had to exhibit similar chemical behaviour (after all, they belonged to a family of notoriously similar elements, the second f family).

Now, what were the actual facts? Thorium at least demonstrated some similarity to cerium but protactinium and uranium had nothing in common with praseodymium and neodymium. The chemical behaviour of the elements Nos. 90, 91 and 92 was such that chemists unhesitatingly classified them as the d elements (the $6d$ elements, to be more precise). Unfor-

tunately, physicists at the time were unable to determine experimentally the electronic structure of such heavy elements.

Therefore, Bohr stated cautiously that if the second “rare-earth family” did exist it had to begin somewhere after uranium. But the transuranium elements were a complete mystery at the time. The first transuranium elements were synthesized in 1940 (neptunium, $Z = 93$, and plutonium, $Z = 94$). They proved to be similar to uranium. Did that mean that the series of the $5f$ elements indeed started with uranium, as suggested by Bohr?

The second “rare-earth family” proves to be unruly. While all lanthanides are typically trivalent, uranium, neptunium and plutonium are not. They can be easily made hexavalent, an unheard-of thing for lanthanides. After the next transuranium elements had been synthesized (americium, $Z = 95$, and curium, $Z = 96$) everything seemed to fall into pattern since these elements had fairly stable trivalent states. That was when the prominent American scientist Glenn Seaborg suggested that the second f family after all started with thorium and named these elements actinides. Seaborg gave the following explanation to the difference in behaviour of the actinides in comparison with the lanthanides. In lighter actinides the $6d$ and $5f$ electron subshells are very close and therefore these atoms, in contrast to lanthanides, have a larger number of electrons capable of forming chemical bonds. Thus, thorium can be tetravalent, protactinium pentavalent and uranium, neptunium and plutonium hexavalent. This is why actinides do not look like the “relatives” of lanthanides.

It was Seaborg who started the tradition of placing

the actinides under the periodic table below the lanthanides. As years went by scientists continued to synthesize new transuranium elements. The names of curium, berkelium, californium, einsteinium, fermium and mendelevium appeared in the periodic table. Then the turn of the elements Nos. 102 and 103 came. Chemists had in their disposal only tiny amounts of new elements but performing highly sophisticated experiments they managed to show that the trivalent state became common in the second half of the actinide series. The ties between the two *f* families became apparently closer. But actinides had more surprises in store....

Trouble again. The alarm was first sounded by the Soviet scientists Nikolai Krot and Anna Gel'man. In 1967 they produced heptavalent neptunium and plutonium (seven years later they added heptavalent americium). The American scientists followed the lead. They demonstrated that the stability of the trivalent state of many actinides at the end of the series was nothing but illusory. They found that the divalent states of fermium, mendelevium and the element No. 102 were amazingly stable and obtained tetravalent californium. Then the Soviet scientists prepared compounds of monovalent mendelevium.

Now we see how wide the range of valence states is as exhibited by the actinides. In comparison, the persistence of the trivalent state among the lanthanides seems quite monotonous.

A critically minded reader will be justified in asking at this point what sense there is in identifying a separate group of actinides as we do with lanthanides. Even Seaborg himself remarked that these two series were not strictly analogous and we have seen that

what similarity remains tends to be eroded with time.

It was only after several decades of hard work that the scientists found a satisfactory placement for the rare-earth elements in the periodic system. Now the matter is more or less settled – though these 15 elements seem crowded in the single lanthanum slot still the generally accepted way of placing the $4f$ elements reflects well the main feature of this series of elements, that is, their great chemical similarity. In contrast, placing 15 actinides into the single actinium slot seems a poor compromise as each actinide has its own specific features and exhibits its own peculiarities of the chemical behaviour which is a constant source of fascination for scientists.

Though other schemes were suggested for placing the $5f$ elements in the periodic table none of them was found acceptable enough for being too artificial.

One comes here to a somewhat unexpected conclusion that it is hardly possible to design an unchallengeable scheme for placing the elements of the second “rare-earth family” in the periodic table. The established structure of the table proves to be too rigid to accommodate the actinides without distorting itself.

Should then the structure be rearranged? No, since the elements of the first six periods fit in it quite consistently and logically. The fact is that the periodic variation of the properties of chemical elements proves to have a much more complicated, intricate and inconsistent character than it was believed several decades ago at the time of great Mendeleev’s discovery.

Here once again we cannot help but be amazed by the wonderful properties of the rare-earth series which is indeed one of a kind in the periodic system of elements.

An ancient wisdom says that everything is understood in comparison. Thus a comparison of lanthanides and actinides has revealed new fascinating aspects of the old family of the rare earths.

The history of the rare-earth chemistry is almost two hundred years old. But enterprising scientists have yet much to learn about it. We wish luck to any of the readers of this book who may happen to become one of them.

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